PREPARATION AND CHARACTERIZATION OF BIODIESEL FROM NON-EDIBLE OILS

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BY

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CERTIFICATE

This is to certify that the work presented in the Thesis, entitled "Preparation and Characterization of Biodiesel from Non-Edible oils" being submitted to National Institute of Technology , Rourkela ,in fulfillment of the requirement for the award of Degree of Doctor of Philosophy(Ph.D.),is an authentic work carried out under our supervision and guidance.

To the best of our knowledge, the content of this Thesis does not form a basis for the award of any previous Degree to any one else.

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Dedicated

To

MY BELOVED PARENTS

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ABBREVIATIONS

1.	**ANN**	**Artificial Neural Network**
2.	**ASTM**	**American Society for Testing and Materials**
3.	**AV**	**Acid value**
4.	**Ai**	**Percentage composition**
5.	**BSFC**	**Brake specific fuel consumption**
6.	**B10**	**10 % Biodiesel +90 % Diesel**
7.	**B20**	**20 % Biodiesel +80 % Diesel**
8.	**B30**	**30 % Biodiesel +70 % Diesel**
9.	**B100**	**100 % Biodiesel**
10.	**D**	**Number of double bond**
11.	**DIN**	**Deutsches Institut für Normung (German Institute for Standardization)**
12.	**FFA**	**Free Fatty Acid**
13.	**FAME**	**Fatty Acid methyl Ester**
14.	**IV**	**Iodine value**
15.	**JOME**	**Jatropha oil methyl ester**
16.	**KOME**	**Karanja oil methyl ester**
17.	**MOME**	**Mahua oil methyl ester**
18.	**MWi**	**Molecular mass of each component.**
19.	**MSE**	**Mean Square Error**
20.	**SN**	**Saponification Number**
21.	**SVO**	**Straight Vegetable Oil**
22.	**x1, x2, x3 and x4**	**Input layer neurons**
23.	**ω_{ij}**	**Weights of a network**

Abstract

Efforts are being made throughout the World to reduce the consumption of liquid petroleum fuels wherever is possible. Biodiesel is recently gaining prominence as a substitute for petroleum based diesel mainly due to environmental considerations and depletion of vital resources like petroleum and coal. According to Indian scenario, the demand for petroleum diesel is increasing day by day hence there is a need to find out an appropriate solution. Under Indian condition only such plants can be considered for bio diesel, which produce non edible oil in appreciable quantity and can be grown in large scale on non cropped marginal lands and waste lands. However, the current utilization of non-edible oilseeds is very low .Bio-diesel has become more attractive recently because of the fact that it is made from renewable resources .Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant . These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a Diesel like fuel, the trans-esterification process was found to be the most viable process.

In the present work, biodiesel has been prepared from edible and non edible oils. As the properties of bio diesel depend on the nature of the vegetable oil used, hence the properties of vegetable oil have also been determined. Some of the properties of vegetable oils have been determined theoretically and compared with the experimental values. Biodiesel have been produced from different edible and non edible oil and the properties of biodiesel produced are measured and compared with those of biodiesel.

As in India the non-edible oil like *Pongamia pinnata* or Karanja oil are available in abundance, which can be converted to biodiesel. Exhaustive studies for the preparation of karanja oil methyl ester (KOME) has been done. Study was carried out with important process variables for optimization of esterification and transesterification reaction to achieve maximum bio diesel production. The important process variables for esterification such as concentration of acid catalyst, alcohol/oil ratio, reaction time, temperature, and % of excess alcohol; and for transesterification; concentration of alkali catalyst, alcohol/oil ratio, reaction time, temperature, % of

excess alcohol are optimized. The results are also verify with artificial neural network (ANN) based method. The results of simulation experiment indicating that the prediction of model of biodiesel yield function is in well agreement with the real process.

Further the performance and emission characteristics of karanja oil, KOME and their various blends with diesel have been studied. Tests were carried out for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emission of CO, CO_2, HC and NOx gases in exhaust. The performance of preheated and blended (lower blend concentrations) Karanja oil are found to be very close to mineral diesel.The test results indicate that the blend fuel B30 can be used in the diesel engines without making any engine modifications. Also the cost of blend fuel (B30) can be considerably reduced than pure diesel. The performance of blended KOME is found to be very close to mineral diesel. It is found that the non edible like Mahua karanja and jatropha oil are also potential raw material for preparation of biodiesel.

Keywords : Straight vegetable oil , Karanja oil, Mahua oil, Jatropha oil, Esterification, Transesterification Karanja oil methyl ester, Mahua oil methyl ester, Jatropha oil methyl ester , Artificial neural network, Brake specific fuel consumption

1. INTRODUCTION

Recent survey on the world energy consumption highlights that a major portion of the total energy consumed is derived from the combustion of fossil fuels. Among the fossil fuels, liquid petroleum based fuels contributes a maximum because of their inherent physicochemical and combustion properties. Unfortunately, the reserves of fossil fuels, specially the liquid fuels are not unlimited and may exhaust, if not utilized economically, within few decades. Efforts are being made throughout the World to reduce the consumption of liquid petroleum fuels wherever is possible. Two general approaches are in use. First is to switch over the energy consumption devices on alternative energy source which are either abundant or are reproducible. The second is to enhance the efficiency of combustion devices. This can be achieved by understanding the physicochemical processes involved during the combustion. Such knowledge is also beneficial in view of propulsion, mitigation of combustion generated pollution and control of fire hazard in handling combustibles.

Recently, there has been a growing concern about the increasing air pollution caused by the combustion of petro diesel. In addition, depleting resources of conventional fuels has caused an increase in its price. Biodiesel is a renewable fuel which is produced from vegetable oil or animal fat through a chemical process and can be used as either direct substitute, extender or as an additive to fossil diesel fuel in compression ignition engines. The most promising feature of biodiesel is that it can be utilized in existing design of diesel engine with no or very little modifications. It has a proven performance for air pollution reduction. Biodiesel is typically produced through the reaction of vegetable oils or animal fat with methanol or ethanol in the presence of catalyst to yield glycerol as major by product[1] (biodiesel chemically called methyl or ethyl ester). However, the price of biodiesel is presently more as compared to petro diesel [2]. Higher cost of biodiesel is primarily due to the raw material cost [3].

1.1 Edible and non edible oil

Biodiesel can be produced either from edible or from non edible. Most of the edible oils are produced from the crop land. The use of edible vegetable oils for bio diesel production has recently been of great concern because they compete with food materials.

Disadvantages of using bio diesel produced from agricultural crops involve additional land use, as land area is taken up and various agricultural inputs with their environmental effects are inevitable. Switching to bio diesel on a large scale requires considerable use of our arable area. If the same thing is to happen all over the world, the impact on global food supply could be a major concern. Currently, more than 95% of the world bio-diesel is produced from edible oil which is easily available on large scale from the agricultural industry. However, continuous and large-scale production of bio diesel from edible oil without proper planning may cause negative impact to the world, such as depletion of food supply leading to economic imbalance. A possible solution to overcome this problem is to use non-edible oil. As the demand for edible oils for food has increased tremendously in recent years, it is urgently required to justify the use of these non edible oils for fuel use purposes such as bio diesel production. Moreover, these oils could be less expensive to use as fuel. Hence, the contribution of non-edible oils such as jatropha and karanja and mahua will be significant as a non edible plant oil source for biodiesel production. Several studies have shown that there exists an immense potential for the production of plant based oil to produce biodiesel. Azam et al. [4] studied the prospects of fatty acid methyl esters (FAME) of some 26 non-traditional plant seed oils including jatropha to use as potential biodiesel in India. Among them, *Azadirachta indica*, *Calophyllum inophyllum*, *J. curcas* and p*ongamia pinnata* were found most suitable for use as biodiesel and they meet the major specification of biodiesel for use in diesel engine. Moreover, they reported that 75 oil bearing plants contain 30% or more oil in their seed, fruit or nut. Subramanian et al. [5] reported that there are over 300 different species of trees which produce oil bearing seeds. Thus, there is a significant potential for non-edible oil source from different plants for biodiesel production as an alternative to petro diesel.

1.1.1. Mahua oil

Bio diesel from mahua seed is important because most of the states of India are tribal where it is abundantly found. The annual production of non edible seed was greater than 2 MT of which mahua is nearly 181 KT **[6].** The major component fatty acids of mahua oil are Palmitic (16-28.2%), Stearic (20-25.1%), Arachidic (0-3.3%), Oleic (41-51%) and Linoleic (8.9-13.7%)**[7]**. Mahua is an nontraditional, non edible oil also known as Indian butter tree. Mahua is a medium to large tree, which may attain a height of up to

20 meters. It is a tree of deciduous nature, of the dry tropical and sub-tropical climate. The tree grows on a wide variety of soils, but prefers sandy soils. As a plantation tree, Mahua is an important plant having vital socio-economic value. This species can be planted on roadside, canal banks etc. on commercial scale and in social forestry programme, particularly in tribal areas. The flowers and fruits are eaten traditionally by tribal people. Mahua oil seed cake can be used as manure.

1.1.2 Jatropha oil

Jatropha curcas is commonly found in most of the tropical and subtropical regions of the world . The oil content of jatropha seed ranges from 30 to 35 % by weight. The fatty acid composition of jatropha oil **[8]** consists of myristic, palmitic, stearic, arachidic, oleic and linoleic acids. After extraction of oil from seed the detoxification of the seed cake is necessary so that the seed cake can be used as cattle feed. Economic development in India has led to huge increases in energy demand, which in-turn has encouraged development of the Jatropha cultivation and Biodiesel production system.

1.1.3 Karanja oil

Karanja is a medium sized tree is found almost throughout India. Karanja tree is wonderful tree almost like neem tree. Pongamia is widely distributed in tropical Asia. Karanja Oil is a nonedible oil of Indian origin . The plant is also said to be highly tolerant to salinity and is reported to be grown in various soil textures viz. stony, sandy and clayey. Major producing country is East Indies, Philippines, and India. Karanja can grow in humid as well as subtropical environments with annual rainfall ranging between 500 and 2500 mm. This is one of the reasons for wide availability of this plant species. The oil content extracted by various authors ranges between 30 to 33% [9]. The cake after oil extraction may be used as manure. Karanja oil has been widely tested for insecticidal and bactericidal activity. In south part of the Indian peninsula the karanja oil/cake are also used same like neem oil and neem cake. The seed oil has been used by the natives of India for hundreds of years. It can be regenerated through direct sowing, transplanting and root or shoot cutting. Its maturity comes after 4–7 years. The oil expelled from the seeds is also burned during the festival of lighting to purify the environment. All these applications are at local or regional level and 94% of the oil from plant is still underutilized.

1.2. Biodiesel processing from vegetable oil

Biodiesel can be produced by esterification followed by transesterfication . The oils and fats are filtered and pre-processed to remove water and contaminants. If, free fatty acids are present, they can be removed or transformed into biodiesel using special pre-treatment technologies. The pre-treated oils and fats are then mixed with an alcohol (usually methanol) and a catalyst (usually sodium methoxide). The oil molecules (triglycerides) are broken apart and reformed into esters and glycerol, which are then separated from each other and purified. The edible oils like soybean, sunflower, mustard, palm, cotton seeds, whose acid values are less than 3.0 are transesterified with methanol in the presence of sodium methoxide as catalyst. Non-edible oil like, Mahua, karanja and jatropha oils having acid values more than 3.0 are undergoes esterification followed by transesterification. The methyl esters produced by these methods are analyzed to ascertain their suitability as diesel fuels.

1.3 Selection of catalyst

Transesterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of mono alcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil [10] **.** The viscocity of esterified oil is lower than the oil. However, higher ratio of alcohol to oil is generally employed to obtain biodiesel of low viscosity and high conversion [11]**.** Alkali-catalyzed transesterification is very fast compared to acid catalyzed [12-13]**.** Methanol and ethanol is widely used in the transesterification because of low cost [14]. The alkali hydrolysis of the oil must have acid value <1 and moisture content of <0.5%. The acid catalyst is the choice for transesterification when low-grade vegetable oil used as raw material because it contains high free fatty acid (FFA) and moisture. Acid catalyst such as sulphuric acid (H_2SO_4) is used for esterification process.

1.4. Performance of biodiesel in diesel engine

A number of studies have shown that biodiesel hold promise as alternative diesel engine fuels [15-22] However, the direct use of vegetable oils and/or oil blends is generally considered to be unsatisfactory and impractical for both direct-injection and indirect type diesel engines. The high viscosity, acid composition, and free fatty acid content of such

oils, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits, and lubricating oil thickening are some of the more obvious problems [23-24]. Consequently, considerable effort has gone into developing vegetable oil derivatives that approximate the properties and performance of hydrocarbon-based diesel fuels. Problems encountered in substituting triglycerides for diesel fuels are mostly associated with their high viscosity, low volatility, and polyunsaturated character [24].Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant [25]. These experiences led to the use of modified vegetable oil as a fuel. There are many ways and procedures to convert vegetable oil into a Diesel like fuel, among them the trans-esterification process was found to be the most viable process [26]. Biodiesel, as an extender for combustion in Diesel engine, has demonstrated a number of promising characteristics, including reduction of exhaust emissions [27]. Transesterified oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of diesel fuel. Its physical and chemical properties required for operation of diesel engine are similar to petroleum based diesel fuel [28]**.** It has been observed that biodiesel can effectively be used as diesel fuel substitute in exiting diesel engine without any engine modification [29].From the investigation it can be concluded that biodiesel can be used as an alternative to diesel in a compression ignition engine without any engine modifications [30]. Just like petroleum diesel, biodiesel operates in compression-ignition engines. Blends of up to 20% biodiesel (mixed with petroleum diesel fuels) can be used in nearly all diesel equipment and are compatible with most storage and distribution equipment.

1.5. Research objectives

The main objective of this work was to study the potential non-edible oils as a source for the production of bio diesel .The properties of bio diesel depends on the nature of the vegetable oil to be used for preparation of bio diesel. In the present investigation, an attempt has been made to produce and characterize different vegetable oil(edible and non edible), bio-diesel from different vegetable oil, optimization of transesterification for the production of biodiesel , engine performance of selected straight vegetable oil , biodiesel and blends of bio-diesel and diesel.

In this study, various properties of different edible oil and their methyl esters are determined experimentally. Physical and chemical properties were determined by using standard test methods. The properties of methyl esters of edible oils are compared with the properties of diesel fuels. The properties of vegetable oil methyl esters have been compared with also with the previous works .In this present work experimental investigations have been carried out to find out the different properties of Mahua, karanja and jatropha oil and their methyl ester. (Mahua Oil Methyl Ester, Karanja oil methyl ester and jatropha oil methyl ester) Kinetic studies to optimize the preparation of a selected non edible Oil , karanja oil methyl Ester (KOME) were carried out varying the different parameters like methanol / oil molar ratio, % of excess alcohol, reaction time, temperature and concentration of acid catalyst. Mahua oil methyl ester (MOME), Jatropha oil methyl ester (JOME) and (KOME) are prepared by using alkali catalyst as sodium methoxide by transesterification process

The bio-diesel is synthesized from different Edible Oil by the process of transesterification. The properties of edible oils like soybean, sunflower, mustard, palm, cotton seeds have been determined by suitable standard methods. Refined edible oils, whose acid values were less than 3.0 were transesterified with methanol in the presence of sodium methoxide as catalyst. The methyl esters produced by these methods were analyzed to ascertain their suitability as diesel fuels.

In the next stage, non-edible oils like karanja, mahua and jatropha and their methyl ester have been chosen to find out their suitability for use as petro-diesel. Experimental investigation has been done to find out the different properties of karanja, mahua and jatropha oil. Theoretical equation has been developed to find out the properties and they have been compared with the experimental values. Biodiesel is prepared from karanja, mahua and jatropha oil, through esterification followed by trans-esterification. The comparison of fuel properties are made between Mahua, Karanja, jatropha oil methyl ester and Diesel. The methyl esters produced by these methods were analyzed to ascertain their suitability as diesel fuels.

In India, non-edible oil like *Pongamia pinnata* or Karanj oil are available in abundance, which can be converted to biodiesel. The non-edible oil is being used in the

soap and pharmaceutical industries, but due to the dark colour and odour of karanja oil, it is less preferable used as compared to other non-edible oil species. Kinetic studies to optimize the preparation of Karanja Oil Methyl Ester (KOME) were carried out varying different parameters like methanol / oil molar ratio, % of excess alcohol, reaction time, temperature and concentration of acid catalyst.

In the next step of optimization, an artificial neural network (ANN) based model for simulation of biodiesel production through the esterification and transesterification of Karanja oil has been developed.

The high viscosity Karanja (Pongamia pinnata) oil was blended with conventional diesel in various proportions to evaluate the performance and emission characteristics of a diesel engine typically used in stationary operation. Diesel, karanja oil fuel blends (10% and 20%) and preheated karanja vegetable oil (At 100^0C and 120^0C) were used to conduct short-term engine performance and emission tests at varying loads. Tests were carried out for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emission of CO, CO_2, HC and NOx gases in exhaust. People of rural and undeveloped areas can use this oil for their agricultural engines without depending on market and without modification of whole engine, at the same time they can reduce the requirement of diesel fuel from outside market.

Biodiesel from karanja oil is produced by alkali catalyzed transesterification process. Performance of C.I engine using karanja oil methyl ester (KOME) blending with diesel and with various blending ratios has been evaluated. The Karanja oil methyl ester (KOME) is blended with conventional diesel in various proportions to evaluate the performance and emission characteristics of a diesel engine typically used in stationary operation. Diesel, KOME blends were used to conduct short-term engine performance and emission tests at varying loads. Tests were carried out for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emission of CO, CO_2, HC and NOx gases in exhaust.

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2. BACKGROUND LITERATURE

2.1. Introduction

Our economy and lifestyle rely on the use of fossil resources for the transportation fuels and materials; however there has been rising concern over their cost, sustained availability, and impact on global warming and pollution [1]. This has led to a search for technologies that generate fuels and materials from renewable carbon sources, such as plant biomass. Depending on the component of the biomass used as feedstock and the technology employed to transform component into desired product, at least three general platforms have been envisioned: the sugar [2], synthesis gas [3], and oil [4] platforms. The sugar and oil platforms are the best established today, with bio ethanol and biodiesel being the examples of their commercial products respectively. Bio ethanol is produced through microbial fermentation of sugar derived from corn, sugarcane or sugar beet [5].

Biodiesel is produced by the transesterification of vegetable oils with alcohols to produce esters. [4].Given the increasing demand for bio fuels [6], there is an urgent need to investigate new and more efficient alternatives for their production. For example, the conversion of lignocelluloses biomass to ethanol and the use of oil accumulating algae in the production of biodiesel are being investigated [7, 8]. These approaches are very promising and will provide abundant non food feedstocks for the production of bio fuels with environmental benefits and large net energy gains. However, an outstanding issue in both current and future biofuel production platforms is economic viability. The implementation of bio refineries has been proposed as a means to increase the economic viability of the biofuel industry [9]. In its 'conventional' form, a bio refinery would make use of a fraction of the feedstock to co – produce a higher value, small – market chemical along with the biofuel. The higher revenue from the co – product, which benefits itself from economies of scale available in a large bio fuels plant, would improve the economics of biofuel production. A more economically viable model for a bio refinery, however should consider the use of byproducts or waste streams generated during the production of biofuel. Glycerol-rich streams generated by the bio fuels industry have the potential to be used in this context. As its name suggests bio diesel is a fuel oil derived from biological sources. Bio-diesel is a domestically produced, renewable fuel that can be manufactured from vegetable oils, animal fats, or recycled restaurant greases and it can replace fossil fuel

[10]. Bio-diesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources [11]. Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions [12]. Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a Diesel like fuel, the trans-esterification process was found to be the most viable oil modification process [13]. More than 100 years ago, Rudolph Diesel tested vegetable oil as the fuel for his engine [14].Although vegetable oils can be used in diesel engines but due to high viscosity, low volatility and poor cold flow properties it causes many problems [15].There are more than 350 oil bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for Diesel engines [16]. Trans-esterification was well known as early as 1864, when Rochleder described glycerol preparation through ethanolysis of castor oil [17-18].

Trans-esterification is the process of using an alcohol (e.g. methanol, ethanol or butanol), in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil, with glycerol as a byproduct. Glycerol is the major value-added byproduct produced from oil and fat from transesterification reactions performed during biodiesel manufacturing processes. Glycerol is liberated at levels of around 10% of the oil or fat and approximately one ton of glycerin is produced for every ten tons of biodiesel. The global amount of glycerin generated from biodiesel is increasing rapidly. Glycerin is most commonly used without modification, or very basic structural modifications, as an additive to materials. Its uses number in the thousands with large amounts being used in the manufacture of food and beverages, tobacco, pharmaceuticals, personal care products, urethane foams, and synthetic resins. Although the personal care industry has seen an increasing demand for glycerin due to consumer desire for eco-friendly “natural” products, the majority of these markets are relatively mature. Absorbing excess glycerin into these markets by replacing petrochemically derived polyols such as ethylene glycol, propylene glycol, and pentaerythritol used in automobile antifreeze, aircraft deicers and alkyd resins

may partially alleviate glycerin surpluses. Currently, industry and government are increasing their efforts to develop new and improve existing glycerol chemistry. Present study focused on importance of SVO, production of biodiesel from different edible and non edible oil.

2.2. Straight Vegetable Oil and Biodiesel

The concept of using vegetable oil as a fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Rudolf Diesel stated: "the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time[19] .Different sources of vegetable oil like soybeans, sunflower seeds, rape seeds, palm, Jatropha, Karanja, Rapeseed can be used in different ways like preheating the oil, blending it with diesel , proved that vegetable oils are feasible substitutes for diesel fuel [20-35]. According to Guibet et al.[36], evaluating a SVO as a diesel fuel reduces to focusing on the viscosity, density, and cloud point. The cloud point of SVOs is strongly related to the fatty acids saturation It has been shown that short-term engine performance is not greatly affected when vegetable oils are used as fuel [37-39]. However, long-term use of straight vegetable oils or in blends with small quantities of diesel fuel has shown some adverse effects on the engine power output, emissions and durability [40-42]. Some of the properties of vegetable oils which influence engine performance have been investigated thoroughly [43-45]. SVO might be the best way to use vegetable oil in diesel engines in the long term as there is no processing required, which makes it the most efficient way to get the oil from the fields to the fuel tank. If vegetable oil is to be significant as one of the future fuels for compression ignition engines it would be necessary to modify fuel injection equipment and combustion chamber design. These changes would be needed to take into account the effects of properties of vegetable oils on the spray characteristics and the subsequent process. Few researchers have worked with feedstock having higher FFA levels using alternative processes [46]. But there are certain exceptional cases wherein direct trans-esterification cannot be performed. Such cases appear in raw vegetables oils (Non edible oil) like karanja , mahua , Nim, Jatropha sal , etc because these raw vegetable oils posses high free fatty acid (FFA). For determining whether the raw vegetable oils can be trans-esterified directly the acid value is the most important property that must be known. If

the acid value is less than 3 then the raw vegetable oil can be directly trans-esterified. If the acid value greater than 3 then there is slight change in the production process. At first the oil undergoes esterification and then followed by trans-esterification. In the esterification process the excess of the free acid gets reacted. The remaining acid content in the oil undergoes trans-esterification. So this method is effective for oils that contain high free fatty acid (FFA) content .Trans esterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of mono alcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil [10]**.** Suitable alcohols include: methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently. Methanol and ethanol is widely used in the transesterification because of low cost [47].This process is widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of fuel and improve engine performance. However, higher ratio of alcohol to oil is generally employed to obtain biodiesel of low viscosity and high conversion [48]**.** Alkali-catalyzed transesterification is very fast compared to acid catalyzed [18, 49]**.** Thus fatty acid methyl ester (also known as biodiesel) is obtained by transesterification and large amounts glycerol is generated as by product.

2.3 Chemistry of Esterification and Transesterification

Esterification is the reaction of an acid with an alcohol in the presence of a catalyst to form an ester. The equation is expressed generally as:

$$RCOOH + R'OH \quad \Leftrightarrow \quad RCOOR' + H_2O$$

Generally, acid catalyst like sulfuric acid is employed. Esterification is a reversible reaction. Thus water produced must be removed to drive the reaction to the right to obtain a higher ester yield.

Transesterification on the other hand is the displacement of the alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. This reaction cleavage of an ester by an alcohol is more specifically called alcoholysis and is represented by the general equation:

$$RCOOR' + R''OH \xrightarrow[CATALYST]{NaOCH_3} RCOOR'' + R'OH$$

In this case, a new ester is formed. Generally alkaline catalysts such as, Sodium hydroxide and Potassium hydroxide can also be used as catalysts.

Transesterification is a general term. More specifically, if methanol is used, the reaction is termed methonolysis. Methanol is generally used because it is cheap, however other alcohols can also be used.

Although the equation reflects the overall reaction, but the reaction usually consists of a series of consecutive reversible steps. For transesterification reaction a large number of potentially useful catalysts have been investigated as a means to enhance the reaction rate. Without added catalysts some degree of rearrangement can be obtained but only under extreme conditions of temperature and time, leading to undesirable effects such as isomerization, polymerization and decomposition. Apart from the generally preferred acid and alkaline catalysts, Sodium Methoxide and Alcolates, have been claimed to catalyze transesterification reactions. This catalyst has the advantages of reducing the reaction time and temperature, used in small quantity without darkening the color of the oil. Transesterification of vegetable oils using methanol and alkaline catalyst is the most commonly used processes for manufacture of methyl esters.

2.4 Process Variables

The most important variables which influence the transesterification reaction are: reaction temperature, ratio of alcohol to vegetable oil, catalyst mixing intensity and purity of reactants.

2.4.1 Reaction Temperature

The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However the reaction is conducted close to the boiling point of methanol (60 – 70 ^{0}C) at atmospheric pressure for a given time. Such mild reaction

conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore degummed and de acidified oil is used as feedstock [12]. Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240 ^{0}C), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60 – 80 ^{0}C at a molar ratio of 6:1 [12-14].

2.4.2 Ratio of Alcohol to Oil

Another important variable is molar ratio of alcohol to vegetable oil. As indicated earlier, the transesterification reaction requires 3 mol of alcohol per mole of triglyceride to give 3 mols of fatty esters and 1 mol of glycerol. In order to shift the reaction to the right, it is necessary to either use excess alcohol or remove one of the products from the reaction mixture. The second option is usually preferred for the reaction to proceed to completion. The reaction rate was found to be highest when 100% excess methanol was used. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher i.e. 98% (w/w)[12].

2.4.3 Catalysts

Alkali metal alkoxides are found to be more effective transesterification catalysts compared to acidic catalysts. Sodium alkoxides are the most efficient catalysts, although KOH and NaOH can also be used. Transmethylation occurs in the presence of both alkaline and acidic catalysts [15]. Being less corrosive to industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5 – 1% (w/w) has been found to yield 94 – 99% conversion to vegetable oil esters [13], and further increase in catalyst concentration does not affect the conversion but adds extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction.

2.4.4 Mixing Intensity

It has been observed that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a

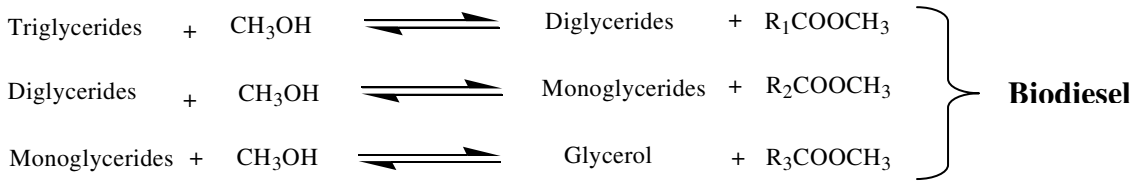
significant role in the slow rate of reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on kinetics of the transesterification process forms the basis for process scale-up and design.

2.4.5 Purity of Reactants

Impurities in the oil affect the conversion level considerably. It is reported that about 65 – 84% conversion into esters using crude vegetable oils has been obtained as compared to 94 – 97% yields refined oil under the same reaction conditions[12]. The free fatty acids in the crude oils have been found to interfere with the catalyst. This problem can be solved if the reaction is carried out under high temperature and pressure conditions.

2.5. Glycerol as By-product of Biodiesel

Glycerol is generated as a by-product during the transesterification of fatty acids to produce biodiesel [50-51]. The tremendous growth of the biodiesel industry created a glycerol surplus that has resulted in a dramatic tenfold decrease in glycerol prices over the past two years. Typical reaction to produce biodiesel is given by the following equation;



During the transesterification reaction about 10 wt% (of fatty acid) glycerol is produced. Production of glycerol is expected to increase with increase in production of bio diesel [52] .Glycerol is a commodity chemical with a multitude of uses [53]. The soap and cosmetic industry constituted 28 % whereas polyglycerols, esters, food and drinks and resale constituted up to 47 % of glycerol utilization. Glycerol is a topic of research recently and the researchers are keen to find out its alternate applications for fuels and chemicals [54-56].The recent developments in the conversion of glycerol into value added products, including citric acid, lactic acid, 1,3-dihydroxyacetone (DHA), 1,3-propanediol (1,3-PD), dichloro-2- propanol (DCP), acrolein, hydrogen, and ethanol *etc.* The versatile new applications of glycerol in the everyday life and chemical industry will improve the economic viability of the biodiesel industry[57].Hong *et al*. [58] conducted the study of

some fundamental problems of lactic acid production from glycerol, aiming at to select a strain suitable for producing high concentration and productivity of lactic acid from glycerol. Glycerol can also find new applications in lubricant manufacturing without very expensivepurification process according to Jerzykiewicz et al. [59].It is also reported that crude glycerol fraction showed remarkable antioxidant and anticorrosive properties determined by electron paramagnetic resonance spectroscopy and Herbert method, respectively[59].

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3. MATERIALS AND METHODS

Materials and methods used in various studies discussed in the following chapter of the thesis are described in this chapter. Various experiments, experimental procedure, experimental set-up , engine set-up and analytical tools used to characterize and to undergo various engine performance test of different vegetable oil (edible and non- edible) and their methyl ester are described.

3.1. Biodiesel processing from vegetable oil

Biodiesel can be produced by a variety of esterification technologies. The oils and fats are filtered and pre-processed to remove water and contaminants. If, free fatty acids are present, they can be removed or transformed into biodiesel using special pre-treatment technologies. The pre-treated oils and fats are then mixed with an alcohol (usually methanol) and a catalyst (usually sodium methoxide). The oil molecules (triglycerides) are broken apart and reformed into esters and glycerol, which are then separated from each other and purified. The edible oils like soybean, sunflower, mustard, palm, cotton seeds, whose acid values were less than 3.0 were transesterified with methanol in the presence of sodium methoxide as catalyst. Non-edible oil like, Mahua, karanja and jatropha oils having acid values more than 3.0 were esterified followed transesterified. The methyl esters produced by these methods were analyzed to ascertain their suitability as diesel fuels.

3.1.1 Catalyst type, concentration and reagents

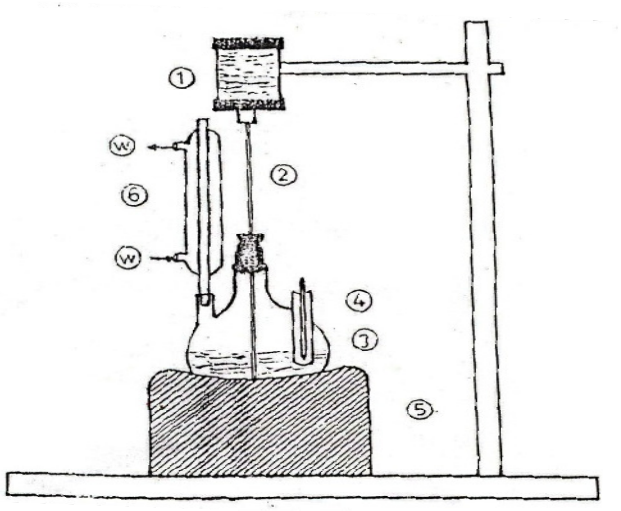
A very large number of potentially useful catalysts have been investigated as a means to enhance the reaction rate. Without added catalysts some degree of rearrangement can be obtained but only under extreme conditions of temperature and time, leading to undesirable effects such as isomerization, polymerization and decomposition .The most common method to produce biodiesel is transesterification of vegetable oils in the presence of a catalyst such as an acid, alkali, or enzyme [1–3]. Apart from the now generally preferred catalysts, e.g. sodium methoxide and alcolates, alkali metal alkoxides are found to be more effective transesterification catalysts compared to acidic catalysts. Sodium alkoxides are the most efficient catalysts, although KOH and NaOH can also be used. Transmethylation occurs in the presence of both alkaline and acidic catalysts [4]. As they are less corrosive to industrial equipment, alkaline catalysts are preferred in industrial processes. A concentration in the range of 0.5-1% (w/w) has been found to yield 94-99%

conversion to vegetable oil esters [5] and further increase in catalyst concentration does not affect the conversion but adds extra cost, as the catalyst needs to be removed from the reaction mixture after completion of the reaction. Transesterification of vegetable oils using methanol and alkaline catalyst is the most commonly used processes for manufacture of methyl esters. This catalyst has the advantages, e.g. short reaction time and relatively low temperature can be used with only a small amount for catalyst and with little or no darkening of colour of the oil. The most important variables which influence the transesterification reaction are: reaction temperature, ratio of alcohol to vegetable oil, catalyst mixing intensity and purity of reactants. Yield of biodiesel is affected by molar ratio, moisture and water content, reaction temperature, stirring, specific gravity etc [6].The non-edible oil with high content of FFAs cannot be directly used in an alkali-catalyzed transesterification process because FFAs react with alkali catalyst to form soaps, resulting in serious emulsification and separation problems. Pre-esterification catalyzed by homogeneous acids, such as sulfuric acid and sulfonic acid, is a conventional and useful method to reduce the content of FFAs, which can turn the raw oil transesterificable by an alkali catalyst and convert FFAs to valuable FAME [7].The literature has revealed that the rate of reaction is strongly influenced by the reaction temperature. However the reaction is conducted close to the boiling point of methanol (60-70°C) at atmospheric pressure for a given time. Such mild reaction conditions require the removal of free fatty acids from the oil by refining or pre-esterification. Therefore, degummed and de acidified oil is used as feedstock [8]. Pretreatment is not required if the reaction is carried out under high pressure (9000 kPa) and high temperature (240°C), where simultaneous esterification and transesterification take place with maximum yield obtained at temperatures ranging from 60-80°C at a molar ratio of 6:1 [8-10]. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher that 98% (w/w) [8-11]. It has been observed that during the transesterification reaction, the reactants initially form a two-phase liquid system. The mixing effect has been found to play a significant role in the slow rate of reaction. As phase separation ceases, mixing becomes insignificant. The effect of mixing on kinetics of the transesterification process forms the basis for process scale-up and design. Impurities in the oil affect the conversion level considerably. It is reported that about 65- 84% conversion into esters using crude vegetable oils has been obtained as

compared to 94-97% yields refined oil under the same reaction conditions [12]. The free fatty acids in the crude oils have been found to interfere with the catalyst. This problem can be solved if the reaction is carried out under high temperature and pressure conditions.

3.1.2 **Experimental set up**

The reactor used for experiments shown in Figure 3.1 is a 1000 ml three-necked round bottom flask. The flask is placed on a heating mantle of 300 watts capacity, whose temperature could be controlled within ±2 ^{0}C. One of the two side necks is equipped with a condenser and the other one is used for thermo-well and for sample collection. A thermometer was placed in the thermo-well containing little glycerol for temperature measurement inside the reactor. The central neck was adapted to a paddle blade impeller with a stirrer. The stirrer rod was passed through the neck using Teflon cap. The motor was connected to a speed regulator for adjusting and controlling the stirrer speed.



1. Electric Motor
2. Stirrer
3. Three-necked Round Bottom Flask
4. Thermo-well with Thermometer
5. Heating Mantle
6. Condenser

Figure 3.1 (a) Experimental set up for the preparation of methyl esters from vegetable oil

3.1.3 Esterification of vegetable oil

A known amount of oil was taken in the above mentioned setup. Heat is supplied to the setup using a heating mantle. A known amount of sulfuric acid in methanol was added to the oil and stirred continuously maintaining a steady temperature of 64^0C. Reaction continued for two hours. Intermittently samples were collected at regular intervals (30 min) and acid values were determined. After the confirmation of completion of the reaction by measuring the acid value of the sample, which should be between 0.1 and 0.5, the heating was stopped and the products were cooled. The un-reacted methanol was separated by distillation. The remaining product is further used for transesterification to obtain methyl esters. The organic layer after neutralizing with 10% NaOH solution, the excess methanol present in the reaction was distilled out. Vacuum was applied to remove the moisture in the sample. The methyl ester was refined with NaOH solution the reaction temperature was maintained at 60^oC for 30 minutes. The refined sample was further cooled and centrifuged to remove residual soap. The organic layer was washed with hot water to neutral Ph. The washed samples was further dried and determined for FFA. The methyl further analysed for determining the properties as per ASTM standards (Table-5). Bound glycerol estimation was performed on the methyl esters to find the unconverted oil. The methyl esters were found to be about 98 % in all the experiments.

3.1.4 Transesterification of Esterified vegetable oil

In a typical experiment a known amount of oil was charged to a three necked round bottom flask (figure 3.1). Solution of known amount of catalyst sodium methoxide was prepared. The solution and the rest required amount of methanol was added to the oil sample. After proper closing of the flask it was put on heating mantle.

The system was maintained at a temperature just above the boiling point of alcohol, i.e. around 70 ^{0}C to speed up the reaction. Recommended reaction time varies from 1 to 2 hours. Excess alcohol was normally used to ensure total conversion of the oil to its esters.

The formation of methyl ester was monitored by using Thin Layer Chromatography technique. Coated silica gel glass plates were spotted with vegetable oil and the sample of ester. The spotted samples were developed in a solvent system in glass chamber using solvent ratio of 80:20 of hexane and ether by volume. This confirms the formation of methyl esters. This procedure was followed for all the samples collected at regular interval time to check the formation of methyl ester. After the confirmation of completion of methyl ester formation, the heating was stopped and the products were cooled and transferred to a separating funnel. The product separated by gravity into two layers namely ester layer and glycerol layer. The ester layer contains mainly methyl ester and methanol and the glycerol layer contains mainly glycerol and methanol. The pH level of both the layers were measured and neutralized separately.

A trace of methanol present in ester layer was recovered in a distillation column under controlled vacuum. Distilled methanol was weighed and stored in sample bottle. Similar procedure was adopted to recover traces of methanol in glycerol layer. The methyl ester obtained was washed and dried under vacuum to remove traces of moisture. A sample of esters was analyzed for acid value by using standard AOCS procedures for standardization. The sample of glycerol layer was analyzed for glycerol content by using AOCS procedure. The glycerol content was found to vary from 80 – 85%.

3.1.5. Glycerol, Sodium Periodate Oxidation Methods (AOCS Method)

This method determines glycerol and other poly alcohols containing three or more adjacent hydroxyl groups. The glycerol reacts with sodium periodate in an acid solution, forming aldehydes and formic acid. The latter is a measure of the glycerol in the sample. The sodium periodate method replaces the acetin method and the dichromate method, because it has been found to be more accurate and more specific for the determination of glycerol as well as being simpler and more rapid.

Reagents used are such as Sodium Periodate solution, NaOH, sulfuric acid, Phenolphthalein indicator, bromothymol blue indicator, ethylene glycol solution, HCl, starch indicator, Potassium iodide solution, and standard Buffer solution.

Procedure:

A known amount of sample containing glycerol is taken in a 600 ml beaker, and dilute with distilled water. Add 5 - 6 drops of Bromothymol blue indicator to the sample in 600 ml beaker, adjust the pH meter to pH 8.1,by adding sulfuric acid/sodium hydroxide solution. Prepare a blank with distilled water in 600 ml as said above in 1 & 2 (with no glycerol).Then add 50 ml Sodium periodate solution with pipette swirl to ensure through mixing and cover with watch glass and allow to stand for 30 mins at room temperature in dark. At the end of 30 mins period, add 10 ml of 50 % ethylene glycol-water solution and allow to stand for 20 mins. Dilute to approximately 300 ml and titrate with NaOH, using PH meter to determine the end point, PH 6.5 for blank, 8.1 for sample.

Calculation Procedure:

$$\text{Glycerol \%} = \frac{(S - B) \times N \times 9.209}{W}$$

Where, S = ml of NaOH solution to titrate sample; B = ml of NaOH solution to titrate blank

N = Normality of NaOH; W = Wt of sample, gms.

Micro Slide TLC:

Clean micro slide (7.5 x 2.5 cm) were coated by dipping two of them together face to face in a slurry of silicagel G (40 gms in chloroform- methanol mixture, 80:20 v/v), and taking out immediately. The coated slides are dried.

Development and Visualisation:

The plates after applying samples as spot were developed with suitable solvent system (Hexane - Ether, 90:10, v/v) in a close glass developing chamber. The separated spots were located by exposing to Iodine vapour.

3.1.6. Bound Glycerol Estimation Analysis

Weigh accurately 50 grams of dried ester sample in a 250 ml round bottom flask. Add a known amount of 15 % aqueous sodium hydroxide solution slowly in to the flask and the content were heated to 80^{o}C for 2 hours in a water bath for saponification. After 2 hours the contents were cooled to room temperature and transferred to a 500 ml beaker and acidulation was performed with a known amount of 1:1 dilute HCl solution. The stirring is continued in a glass beaker with a help glass rod. For at least 5 minutes. After 5 Minutes the contents were separated in to a separating funnel and the acid layer was completely removed and weighed. After weighing equal amount of acid layers is transferred in two beakers and it is diluted with water. Further the sample is analysed for % glycerol content by AOCS methods.

3.2. Optimization of Estrification and transesterification process parameters for the production of biodiesel from Karanja oil

3.2.1 Laboratory Tests to Perform the Optimization of the Esterification and Trans-esterification Process.

Raw karanja oil is selected as a raw material. Biodiesel can be produced by a variety of esterification technologies. The oils and fats are filtered and pre-processed to remove water and contaminants. If, free fatty acids are present, they can be removed or transformed into biodiesel using special pre-treatment technologies. Non-edible oil like karanja oils having acid values more than 3.0 were esterified followed transesterified.

Esterification is the reaction of an acid with an alcohol in the presence of a catalyst to form an ester. The equation is expressed generally as:

Acid catalyst

RCOOH	+	R'OH	⇔	RCOOR'	+	H_2O	**(1)**
Free fatty acid		Alcohol	H_2SO_4	Methyl ester		Water	

Generally, acids catalysts like sulfuric acid are employed. Esterification is a reversible reaction. Thus water must be removed to drive the reaction to the right to obtain a higher ester yield. Transesterification on the other hand is the displacement of the alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is used instead of water. This reaction cleavage of an ester by an alcohol is more specifically called alcoholysis and is represented by the general equation:

Overall reaction as: -

$$\begin{array}{lcccccl} R_1COOCH_2 & & & \textbf{catalyst} & HOCH_2 & R_1\,COOCH_3 & \\ R_2COOCH & + & 3CH_3OH & \Leftrightarrow & HOCH & + \; R_2COOCH_3 & \textbf{(2)} \\ R_3COOCH_2 & & & \textbf{Sodium} & HOCH_2 & R_3COOCH_3 & \end{array}$$

Triglyceride (TG) Alcohol Methoxide Glycerol Methyl esters (Biodiesel)

In this case, a new ester is formed. Generally alkaline catalysts are used. In case of esterification, a new ester is created from free fatty acids, thus it is called esterification (pretreatment).In the second reaction, a triglyceride is converted into three individual esters, which is known as transesterification. Transesterification reactions can be base-catalyzed, acid catalyzed, or enzymatic. Esterification is an acid catalyzed reaction; otherwise free fatty acids convert into soap in base catalyzed reaction forming water molecules and salts, which act as barrier to the ester layer separation, this process is called as saponification.

In case of esterification processes the karanja oil is preheated at different temperature and then the solution of sulfuric acid and methanol is added to the oil and stirred continuously at different temperature. Esterification is continued till the acid value was lowered and remained constant. (Which should be between 0.1 and 0.5) Then the heating was stopped and the products were cooled. The un-reacted methanol was separated by distillation. The remaining product was further used for transesterification to obtain methyl esters.

To carry out the optimization of the esterification process, the parameters involved in the process are identified. The most important parameters are the amount of catalyst (sodium methoxide), methanol / oil molar ratio, percentage of excess alcohol and reaction

time. The rest of the parameters affecting the esterification and transesterification process are considered to have a lower impact on the results and are discarded. Then, the optimum value of each selected variable is found, while the rest of the parameters remained constant.

3.2.2. ANN Methodology to Simulate Esterification and Transesterification Performance.

The simulation model is performed by means of a multilayer perceptron network, which is chosen because it is one of the most elementary forms of neural network structures [13].

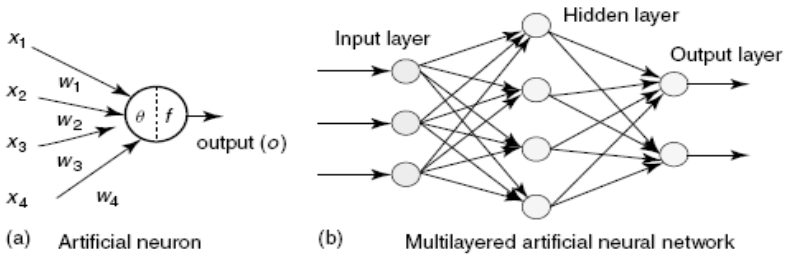


Figure 3.2. Multilayer perceptron model

In the present work an artificial neural network (ANN) based program is developed on MATLAB platform . As shown in Figure 3.2, the multilayer perceptron consists of artificial neurons that constitute the input, the hidden, and the output layers of the neural network model. The input nodes forward the values of the input variables to the hidden layer, and the output nodes produce the final model estimations. The next step consisted of ANN training. The learning rule of an ANN, also called the training algorithm, is a procedure for modifying the weights of a network, $\boldsymbol{\omega}_{ij}$, to decrease the error between the estimated values and the experimental output. In the present study, the Conjugate gradient algorithm, which is a nonlinear least-squares algorithm applied to the learning of the multilayer perceptrons, is applied and chosen to establish the weight assignment.The basic back propagation algorithm adjusts the weights in the steepest descent direction (negative of the gradient), the direction in which the performance function is decreasing most rapidly. It turns out that, although the function decreases most rapidly along the negative of the gradient, this does not necessarily produce the fastest convergence. In the conjugate gradient algorithms a search is performed along conjugate directions, which produces generally faster convergence than steepest descent directions. In most of the training

algorithms discussed up to this point, a learning rate is used to determine the length of the weight update (step size). In most of the conjugate gradient algorithms, the step size is adjusted at the each iteration. A search is made along the conjugate gradient direction to determine the step size that minimizes the performance function along that line. The paper introduces a conjugate gradient method which avoids the line-search per learning iteration.

To prevent overtraining, a technique called cross-validation is also used. Overtraining is the situation in which the network memorizes the data of the training set but generalizes poorly. Although the network is not trained with the cross-validation set, it used the cross-validation set to choose the best set of weights. To perform the cross-validation method, the data set is separated into two sets, called the training set (also divided into the training subset and the validation subset) and the testing set (drawn with the rest of the patterns). Learning is performed on the training set, and then, the validation subset was used to evaluate the quality of the result. Finally, when the error was adequate, the test set is used for prediction and final error measure. The test set is reserved to assess the final performance measure (generalization).During the training phase, the Conjugate gradient method is applied to the training set for at least 500 epochs for estrification and 1200 for transesterification, and the error of the validation set is tested. Then, to determine the feasibility of the new set of weights, the error of the testing subset is computed. The process is repeated until the residual between the model output and the desired output decreased and the model learned the relation between the input and the output.

3.2.2.1. Determining the Number of layers of the Perceptron and the Number of Neurons.

The first step of the process is to find the number of layers, the number of neurons in the layers, and the type of neurons or activity function that correlates input and output. The most appropriate forms of the activity function were found to be a hyperbolic tangent function for the hidden layer and a linear transfer function for the output layer. The relationship between the input and the output of the ANN is shown in **(3)** ;

$$f(n) = [2 / (1 + e^{-2n})] - 1] \quad \textbf{(3)}$$

Where the input to neuron j in layer k is

$$i_j^k = \Sigma_i w_{j,i}^k \, o_i^{k-1} + b_j^k, \quad k = 1{:}2 \quad \textbf{(4)}$$

Where *b* is the bias and the output from neuron *j* in layer *k* is

$$o_j^0 = \quad xj \qquad \textbf{(5)}$$

$$o_j^k = f(i_j^k),\ k = 0{:}2 \qquad \textbf{(6)}$$

As previously mentioned, the selected ANN is a multilayer perceptron network, with three layers of neurons (an input layer, one hidden layer, and an output layer).In case of esterification the number of input layer neurons is three and consists of (Figure 1) the temperature (*x1*), the % of catalyst (*x*2) and the reaction time (*x*3). This set of variables constitutes the input data vector of the proposed multilayer perceptron. One output layer neuron, Esterified Oil (EO), was determined in all cases, while the number of hidden neurons is determined by a heuristic procedure. In case of trans esterification the number of input layer neurons is four and consists of the methanol to oil ratio (*x1*), the reaction time (*x*2),Excess alcohol(*x*3) and the % of catalyst (*x*4) . This set of variables constitutes the input data vector of the proposed multilayer perceptron. One output layer neuron, Biodiesel produced (y), is determined in all cases, while the number of hidden neurons was determined by a heuristic procedure. This procedure consisted of testing different number of neurons, where the mean error of the output data for a small number of iterations in the batch training algorithm was verified. To perform the modeling technique, a set of input-output data is required. The convergence criterion consisted of minimizing the mean squared error, which is the difference between the neuron response and the corresponding correct (target) output, to a value less than 10^{-3}.

In the present work an artificial neural network (ANN) based program is developed on MATLAB platform .As we have the training data set of esterification and transesterification, ANN has been used for predicting the value for unknown value. Standard Back propagation algorithm[14] has been used for training the ANN.

3.3. Performance and emission analysis of preheated and blended karanja oil

The typical engine used for stationary application has been selected for present experimental investigation. A single cylinder, four strokes, constant speed, water-cooled, direct injection diesel engine is used for the experiments. The technical specification of the

engine is given in Table.3.1 .The engine operated at constant speed of 1500 rpm. The fresh lubricating oil 20W40 is filled in oil sump before starting the experiments. The engine is coupled with single-phase 230V AC alternator with water rheostat loading. The main components of the experimental setup are two fuel tanks (Diesel and Karanja oil). The schematic layout of the experimental set up is shown in Fig.3.3.

3.3.1. Working Procedure

KOME is taken and preheated in an isothermal batch reactor to evaporate small traces of moisture. Then the KOME is blended with diesel in the different ratios. A 4 – stroke single cylinder diesel engine has been setup in the tank of which the blends of KOME is poured one by one. Load is given in terms of 0.25 kW starting from zero loads. The corresponding voltmeter and ammeter readings were taken for each sample. The speed in revolutions per minute (rpm) of the diesel engine is noted down using a Tachometer.For every 10 cc rise in the oil level in the burette, the corresponding time has been noted down. From these data, the values of TFC, BP, η_{mech}, $\eta_{Bth,}$ has been calculated using different formulae

Table.3.1 - Engine specification

Manufacturer	Kirloskar oil Engine Ltd, India
Engine Type	Vertical,4 stroke, single cylinder, constant speed, direct injection, water cooled, compression ignition engine with electrical dynamometer
Rated power	5hp at 1500 rpm
Piston diameter & stroke length	0.08m and 0.11m
Compression Ratio	16:1
Nozzle pressure	200kg/cm^2

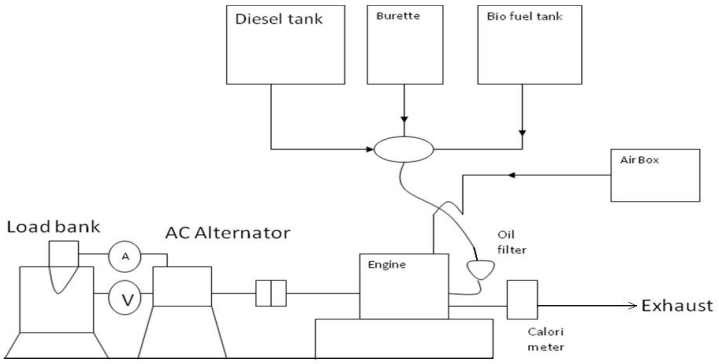


Figure 3.3 (a) Schematic diagram of experimental set up

Figure 3.3 (b) Four stroke Diesel Engine

3.3.2. Engine Performance test and emission analysis of Karanja oil and its blend with diesel

The engine performance tests are conducted with the engine set up (Fig 3.3). The engine tests are carried out using diesel, diesel blends with karanja oil, preheated karanja oil at 100^0C and 120^0C . Performance is evaluated in terms of specific fuel consumption, break thermal efficiency and exhaust temperature.

3.4. Performance and emission analysis of Karanja oil methyl ester (Bio diesel)

The typical engine used for stationary application has been selected for present experimental investigation. A single cylinder, four strokes, constant speed, water-cooled, direct injection diesel engine is used for the experiments. The technical specification of the engine is given in Table.3.1 .The engine operated at constant speed of 1500 rpm. The fresh lubricating oil 20W40 was filled in oil sump before starting the experiments. The engine

is coupled with single-phase 230V AC alternator with water rheostat loading. The main components of the experimental setup are two fuel tanks (Diesel and Karanja oil methyl ester). The schematic layout of the experimental set up is shown in Fig.3.3.

The engine tests are carried out in two phase

3.4.1. Engine Performance test and emission analysis of KOME and its blend with diesel

The engine performance tests were conducted with the engine set up (Fig 3.3). The engine tests were carried out using diesel, diesel blends with KOME. Performance is evaluated in terms of specific fuel consumption, break thermal efficiency and exhaust temperature.

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4. PRODUCTION OF BIODIESEL FROM EDIBLE OILS

4.1. Introduction

The energy in biomass from plants or wastes that they produce originally comes from solar energy through the photosynthesis process. The energy productions from vegetable oils seem to be attractive based on bioresource sustainability, environmental protection and economic consideration. In recent years, many studies have investigated the economic and environmental impacts of the biofuels, especially bio ethanol, biodiesel, biogas, and biohydrogen [1–3]. Most current research on biorenewable fuel is considerably focused on producing biodiesel from vegetable oils [4–5].Biodiesel (fatty acid methyl ester) which is derived from triglycerides by transesterification with methanol has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel. By way of transesterification, the reaction of triglycerides with alcohol (e.g. methanol) under the caustic catalyst is processed to produce glycerol and monoalkyl esters [6–11], which are known as biodiesel and can be potentially used as alternative diesel fuels in compression-ignition (diesel) engines [12–15].

Biodiesel is recently gaining prominence as a substitute for petroleum based diesel mainly in western countries due to environmental considerations and depletion of vital resources like petroleum and coal. The possible use of renewable resources as fuels and as a major feedstock for the chemical industry is currently gaining acceptance. Further as petroleum is a fast depleting natural resource, an alternative renewable route to petroleum is deemed necessity. Traditionally the collection and selling of tree-based oilseeds was generally carried out by poor people for use as fuel for lighting. Presently there is an extended use of these oils in soaps, varnishes, lubricants, candles, cosmetics, etc. However, the current utilization of non-edible oilseeds is very low. Despite the fact that neat edible oil competes with food supply, it is the feedstock that allows the simplest conversion method. The edible oil crop plantation has already been well established and also it is observed that, some crops producing high quality oil that gives highest conversion through the transesterification reaction. Proper management on the oil supply is required so that oil for food consumption and for consumer products is guaranteed and the remaining oil can be converted into biodiesel. A sustainable plantation is comprehensive practices that maintain the benefits to the environment, people, and profitability [16]. To illustrate the practice of

sustainable plantation, a case study is presented from the palm oil plantation in Malaysia. Palm oil is currently the largest supply of edible oil in the world with Malaysia being the largest producer [17, 18]. Palm oil has dominated the world's vegetable oil demand because of its versatile applications ranging from food to consumer products, and now as biodiesel.

Methyl esters are non-corrosive and are produced at lower operating pressure and temperature conditions. Concentrated (about 80%) glycerin is obtained as byproduct during transesterification process. Leyes [19] has shown the effect of alcohol to oil ratio on the yield of ester at equilibrium when the reaction is carried out homogeneously. Bradshaw [20] stated that 4:8:1 molar ratio of methanol to vegetable oil leads to 98% conversion. He noted that ratio greater than 5.25:1 interfered with gravity separation of the glycerol and added useless expense to the separation. Freedman, et al [21] studied the effect of molar ratio of methanol to oil and effect of changes in concentration of tri-, di- and monoglycerides on ester yield. They used four different oils namely soybean, sunflower, peanut and cottonseed oils varying the molar ratio of methanol to oil from 3:1 to 6:1 and concluded that 98% conversion was obtained at a molar ratio of 6:1.

There are large number of commercial plants producing biodiesel by transesterification of vegetable oils and fats based on base catalyzed (caustic) homogeneous transesterification of oils. However, homogeneous process needs steps of glycerol separation, washings, very stringent and extremely low limits of Na, K, glycerides and moisture limits in biodiesel [22].The present report is review of the progress made in development of heterogeneous catalysts suitable for biodiesel production. This review shall help in selection of suitable catalysts and the optimum conditions for bio diesel production.

Several processes for biodiesel fuel production have been developed, among which transesterification using alkali as catalyst gives high level conversion of triglycerides to their corresponding methyl ester in a short duration. This process has therefore been widely utilized for biodiesel fuel production in a number of countries. In the present studies, the properties of edible oils like soybean, sunflower, mustard, palm, cotton seeds have been determined by suitable standard methods. Refined edible oils, whose acid values were less than 3.0, were transesterified with methanol in the presence of sodium methoxide as catalyst (Chapter 2, Biodiesel processing from Edible oil). The methyl esters produced by these methods were analyzed to ascertain their suitability as diesel fuels.

4.2. Results and discussion

Various physical and chemical properties of edible oils and their esters are determined experimentally according to the methods listed in Table 4.1. These standard values were calculated according to USA (ASTM), Germany (DIN), India (BIS) and European Organization (EN). The values of different properties of edible oils are given in Table 4.2. As acid values of edible oils are less than 3.0, hence only transesterification has been done to prepare biodiesel from them. The properties of methyl esters of edible oils are given in Table 4.3 and they have been compared with the properties of diesel fuels.

The properties of vegetable oil methyl esters have been compared with the previous works in Tables 4.4 to 4.7. The properties of Sunflower Methyl Esters **,** Soybean Methyl Esters, Palm Methyl Esters and Mustard Methyl Esters are compared with previous work [23-27].

It is observed that the quality of biodiesel produced here are comparable with that of others and also with diesel fuel. It is also observed that the specific gravities of vegetable methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these methyl esters in range of 37 to 40 MJ/kg, are slightly lower as compared to diesel fuel (42.1 MJ/kg). The fuel properties of vegetable methyl esters were also within biodiesel specifications.

Table. 4. 1: Standard Methods

Test Property	AOCS Method
Acid Value (mg KOH/gm)	Cd 3d – 63
Saponification Value (mg KOH/gm)	Cd 3 – 25
Iodine Value	Cd 1 – 25
Free Glycerin (wt %)	Ca 14 – 56
Total Glycerin (wt %)	Ca 14 – 56
Density (mg/lit)	Cc 10a – 25
Conversion (%)	------
Flash Point (^{0}C)	[ASTM] D92
Pour Point (^{0}C)	[ASTM] D97
Cloud Point (^{0}C)	[ASTM] D2500
Viscosity (c St) at 40 ^{0}C	[ASTM] D445
Heating Value (MJ/kg)	IS:1350
Cetane Index	[ASTM] D976
Ash Content (wt %)	[ASTM] D5347 – 95

Table 4.2: Properties of Edible Oils

Properties	Sunflo-wer Oil (Refined)	Soybean Oil (Refined)	Palm Oil (Refined)	Mustard Oil (Refined)	Cotton Seed Oil (Refined)
Acid Value (mgKOH/gm)	0.04	0.1205	0.1054	0.261	0.111
Saponification Value (mgKOH/gm)	191.86	193.03	197.35	178.30	191.00
Iodine Value	133.27	136.67	52.41	100.99	110.65
Phosphorous Content (ppm)	13.50	NIL	NIL	NIL	NIL
Peroxide Value (milli.eq/kg)	0.50	0.45	1.01	0.89	0.55
Density (g/ml)	0.916	0.919	0.899	0.910	0.917

Table 4.3: Properties of Various Bio-diesels Prepared

Properties	Sunflower Oil Methyl Ester	Soybean Oil Methyl Ester	Palm Oil Methyl Ester	Mustard Oil Methyl Ester	Cotton Seed Oil Methyl Ester	Diesel
Free Fatty Acid	0.0675	0.07	0.096	0.230	0.0113	----
Acid Value (mg KOH/gm)	0.135	0.1405	0.1921	0.461	0.227	----
Saponification Value (mg KOH/gm)	193.36	191.50	196.22	175.75	188.38	----
Iodine Value	135.66	134.90	54.55	101.3	108.4	----
Free Glycerin (wt %)	0.011	0.015	0.014	0.009	0.012	---
Total Glycerin (wt %)	0.0381	0.0575	0.064	0.0292	0.0612	----
Conversion (%)	98.0	97.1	97.52	98.65	97.35	----
Flash Point (^{0}C)	183	180	164	170	162	74
Pour Point (^{0}C)	– 4	– 6	8	– 9	– 8	– 16
Cloud Point (^{0}C)	1	0	13	– 2	– 1	– 12
Density (mg/lt)	0.860	0.880	0.875	0.850	0.857	0.85
Viscosity (c St) at 40 ^{0}C	4.22	4.0	4.42	4.71	4.32	2.98
Heating Value (MJ/kg)	36.5	37.1	37.0	39.62	38.72	42.9
Cetane Index	44.0	44.5	61.84	54.56	50.88	49.2
Ash Content (wt %)	0.005	0.008	0.012	0.01	0.004	0.02

Table 4.4: Comparison of Properties of Sunflower Methyl Esters

Test Property	*Sunflower Methyl Ester*	*Antolin et al* **[23]**	*Fukuda et al* **[24]**
Free Fatty Acid	0.00675	0.015	-----
Acid Value (mg KOH/gm)	0.135	0.3	-----
Saponification Value (mg KOH/gm)	193.36	-----	-----
Iodine Value	135.66	-----	-----
Free Glycerin (wt %)	0.011	-----	-----
Total Glycerin (wt %)	0.0381	-----	-----
Conversion (%)	98.0	-----	-----
Flash Point (^{0}C)	180	-----	183
Pour Point (^{0}C)	– 4	-----	-----
Cloud Point (^{0}C)	1.0	1.0	1.0
Density (mg/lit)	0.860	0.886	-----
Viscosity (c St) at 40 ^{0}C	4.22	-----	4.6
Heating Value (MJ/kg)	37.5	40.0	33.5
Cetane Index	44.0	46.9	49
Ash Content (wt %)	0.005	0.004	-----

Table 4.5: Comparison of Properties of Soybean Methyl Esters

Test Property	*Soybean Methyl Ester*	*Clark et al* **[25]**	*Fukuda et al* **[24]**
Free Fatty Acid	0.007	-----	-----
Acid Value (mg KOH/gm)	0.1405	-----	-----
Saponification Value (mg KOH/gm)	191.5	-----	-----
Iodine Value	134.9	-----	-----
Free Glycerin (wt %)	0.015	-----	-----
Total Glycerin (wt %)	0.0575	-----	-----
Conversion (%)	97.1	-----	-----
Flash Point (^{0}C)	180	141	178
Pour Point (^{0}C)	– 6	– 1	-----
Cloud Point (^{0}C)	0	2	1
Density (mg/lit)	0.88	0.884	0.885
Viscosity (c St) at 40 ^{0}C	4.0	4.08	4.5
Heating Value (MJ/kg)	37.1	39.8	33.5
Cetane Index	44.5	46.2	45.0
Ash Content (wt %)	0.008	0.01	-----

Table 4.6: Comparison of Properties of Palm Methyl Esters

Test Property	*Palm Methyl Ester*	*Mohamad et al* **[26]**	*Fukuda et al* **[24]**
Free Fatty Acid	0.096	-----	-----
Acid Value (mg KOH/gm)	0.1921	-----	-----
Saponification Value (mg KOH/gm)	196.22	-----	-----
Iodine Value	54.55	-----	-----
Free Glycerin (wt %)	0.014	-----	-----
Total Glycerin (wt %)	0.064	-----	-----
Conversion (%)	97.52	-----	-----
Flash Point (^{0}C)	164	109	160
Pour Point (^{0}C)	8	0	-----
Cloud Point (^{0}C)	13	0	13
Density (mg/lit)	0.875	0.8737	0.879
Viscosity (c St) at 40 ^{0}C	4.42	14.94	5.7
Heating Value (MJ/kg)	37.0	39.3	-----
Cetane Index	61.84	-----	62
Ash Content (wt %)	0.012	-----	-----

Table – 4.7: Comparison of Properties of Mustard Methyl Esters

Test Property	*Mustard Oil Methyl Ester*	*Srivastava et al* **[27]**
Free Fatty Acid	0.23	0.24
Acid Value (mg KOH/gm)	0.461	0.456
Saponification Value (mg KOH/gm)	175.75	193
Iodine Value	101.3	90
Free Glycerin (wt %)	0.009	-----
Total Glycerin (wt %)	0.0292	-----
Conversion (%)	98.65	-----
Flash Point (^{0}C)	170	107
Pour Point (^{0}C)	– 9	– 6
Cloud Point (^{0}C)	– 2	-----
Density (mg/lit)	0.85	0.85
Viscosity (c St) at 40 ^{0}C	4.71	5.7
Heating Value (MJ/kg)	39.62	39.82
Cetane Index	54.56	47
Ash Content (wt %)	0.01	-----

4.3. Conclusion

In the present study, it is observed that the quality of biodiesel produced here are comparable with that of others and also with diesel fuel. It is also observed that the specific gravities of vegetable methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these methyl esters are slightly lower as compared to diesel fuel. The fuel properties of vegetable methyl esters were also within biodiesel specifications.

This study suggests that the vegetable oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and/or transesterification. The biodiesel from refined vegetable oils meets the Indian requirements of high speed diesel oil. But the production of biodiesel from edible oils is currently much more expensive than diesel fuels due to relatively high cost of edible oils. There is a need to explore non-edible oils as alternative feed stock for the production of biodiesel. Non-edible oils such as Karanja (Pongamia Pinnata), Jatropha (Jatropha Curcas), Mahua (Madhuca Indica), Undi (Calophyllum Inophyllum), etc. are easily available in many parts of the world including India and are very cheap compared to edible oils. Production of these oil seeds can be stepped up to use them for production of biodiesel.

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5. PREPARATION AND CHARACTERIZATION OF BIO DIESEL FROM NON EDIBLE OIL

5.1. Introduction

There has been greater awareness on biodiesel in developing countries in the recent times and significant activities have picked up for its production especially with a view to boost the rural economy. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel. The use of non-edible oils when compared with edible oils is very significant in developing countries because of the tremendous demand for edible oils as food, and they are far too expensive to be used as fuel at present [1].Throughout the world, large amounts of non-edible oil plants are available in nature [2].The production of biodiesel from different non-edible oilseed crops has been extensively investigated over the last few years. Some of these non-edible oilseed crops include jatropha tree (Jatropha curcas) [3-4], karanja (Pongamia pinnata) [5-6], rice bran [7-8], mahua (Madhuca indica) [9-10], castor [11], linseed [12] and algae [13-14], etc. Conversion of these types of non-edible oil into biodiesel is comparable in the process and quality to other edible oils [15].

In the last few years interest and activity in bio diesels has grown dramatically across the globe. The use of edible oil to produce bio diesel in India is not feasible in view of big gap in demand and supply of such oil. In India, as edible oils are in short supply, non-edible oil like karanja, Jatropha , Mahua, are being considered as the source of SVO and biodiesel.In the present investigation non-edible oils like mahua , jatropha , karanja, and their methyl ester have been chosen to find out their suitability for use as petro-diesel. Experimental investigation has been done to find out the different properties of mahua, jatropha and karanja,oil. Theoretical equation has been developed to find out the properties and they have been compared with the experimental values. Biodiesel is prepared from karanja, mahua and jatropha oil, through esterification followed by trans-esterification. Esterification was performed using acid catalyst (5% H_2SO_4) and methanol The transesterification reaction was carried out alkali catalyst (sodium methoxide) and

methanol. The comparison of fuel properties are made between mahua, karanja, jatropha oil methyl ester and Diesel. The various properties of methyl esters are found to be comparable with that of diesel fuel. The methyl esters produced by these methods were analyzed to ascertain their suitability as diesel fuels.

5.2. Characterization of Mahua, Karanja and Jatropha oil and their methyl ester

Physical and chemical properties were determined by using standard test methods. These standard values were calculated and compared with USA (ASTM D6751), Germany (DIN 51606), India (BIS) and European Organization (EN 14214). Flash point, fire point, viscosity, cloud points, pour point (PP), cetane number, carbon residue, acid value, iodine value**,** saponification number (SN), etc. had been determined [16-20]. Theoretical and experimental value of important chemical properties like acid value, saponification value and iodine value of jatropha oil were calculated by following equation:

Experimental:

Acid value = (No. of ml of N/10 KOH used * 5.6) / mass of oil in gram

Saponification value = (No. of ml of N/2 KOH taken **–** No. of ml of N/2 acid used in back titration) * 28 / mass of oil in gram.

Iodine value = IV = (Difference of ml. of the titration value of blank and the sample * 1.27) / mass of oil taken in gram

Theoretical:

Saponification value SN= $\sum$ (560 × Ai) / MWi, Iodine value IV =$\sum$ (254 × D × Ai) /MWi, Where Ai = percentage composition, D = No. of double bond, MWi = Molecular mass of each component.

5.3. Results and Discussion

5.3.1. Characterization of edible and non-edible oil

In the present work a comparison is made between Theoretical and Experimental value of important chemical properties like acid value, saponification value and iodine value of non edible oil. A comparison is also made between different edible and non edible oil. The details are given in table 5.1. The theoretical values are in well agreement with

their experimental values indicating that if the composition of vegetable oils is known, we can find out their properties by theoretical equations within agreeable error.

Table 5.1: Comparison of experimental and theoretical value of different properties of vegetable oil

Vegetable oil	Experimental saponification value	Theoretical saponification value	Experimental Iodine value	Theoretical Iodine value	Experimental Acid Value	Theoretical Acid value
Soyabean oil	139-195	199.172	127-138	123	195-205	198.
Coconut oil	210-216	206.522	95	99	260-270	258
Corn oil	187-193	191.45	103-128	115	195-203	208
Palm oil	105-110	106.45	97	95	190-210	218
Rapseed oil	315.2	298.45	94.2	98	180-210	215
Linseed oil	189-195	188.12	165-205	170	197-204	181
Jatropha oil	196-200	199.24	96-105	101	5.31	8
Karanja oil	186-196	190	80-90	96	20	24
Mahua oil	190-195	191	60-65	63	18.38	27

5.3.2. Characterization of Mahua oil and Mahua oil Methyl Ester:

A comparison of fuel properties are made between Mahua Oil, Mahua Oil Methyl Ester and Diesel in table 5.2 and it is found that the reduction of viscosity is about 60-65%. Mahua Oil Methyl Ester has calorific value 5% lower than diesel fuel. Kinematic viscosity and cetane value slightly higher than diesel. This is favorable for combustion. Flash point and Fire point are high, which is an advantage for fuel transportation. The various properties of Mahua Oil Methyl Ester (MOME) are found to be comparable with that of the Diesel fuel. Properties of bio diesel depend on the nature of the vegetable oil to be used for preparation of bio diesel by esterification and/or trans-esterification.

Table 5.2. Comparison of Fuel properties of Mahua oil, Mahua oil methyl ester diesel

Property	Diesel oil	Mahua oil	MOME	ASTM D6751-02	DIN EN14214
Density (15^0C), kg/m^3	835	945	872	875-900	860-900
Kinematic Viscosity, 40^0 C, mm^2/s	2.4	25	4.0	1.9-6.0	3.5-5.0
Flash point, ^{0}C	70	226	204	>130	>120
Fire point, ^{0}C	76	250	230	>65	>70
Cloud point, ^{0}C	-10 to-15	14	6	Summer = 4 Winter = -1	Summer = 6 Winter = 1
Pour point, ^{0}C	-35 to -15	15	1	----	-----
Acid value, mg of KOH/g oil	NM	30	0.5	< 0.8	<0.5
Calorific value (MJ/Kg)	43	35	41	40 Min	49 Max
Saponification value	NM	191	130	----	----
Colour	Light brown	Slight greenish yellow	Dark yellow	-----	-----
Cetane number	47	NM	50	----	----
Aniline point, ^{0}C	69	60	63	----	-----
Iodine value	NM	65	60	----	------

5.3.3. Characterization of Jatropha oil and Jatropha oil Methyl Ester

The fuel properties of jatropha oil, jatropha oil methyl ester and diesel were compared and given in Table 5.3. From the various properties, it is found that the calorific values of these methyl esters are 37.2mj/kg, which is low, compared to diesel fuels (42.0 MJ/ Kg). Kinematic viscosity and cetane values are slightly higher than diesel, which is favorable for combustion. Higher flash point is advantageous for fuel transportation. The various properties of jatropha oil methyl ester found to be comparable with that of diesel fuel.

Table 5.3: Comparison of Fuel properties of Jatropha oil, jatropha methyl Ester and diesel

Property	Unit	Jatropha oil	Jatropha Oil Methyl Ester	Diesel	ASTM D 6751-02	DIN EN 14214
Density at 15 °C	kg/m^3	918	880	850	875-900	860–900
Viscosity at 40 °C	mm^2/s	35.4	4.84	2.60	1.9–6.0	3.5–5.0
Flash point	°C	186	162	70	>130	>120
Pour point	°C	-6	-6	–20	--	--
Water content	%	5	Nil	0.02	<0.03	<0.05
Ash content	%	0.7	Nil	0.01	<0.02	<0.02
Carbon residue	%	0.3	0.025	0.17	–	<0.3
Sulphur content	%	0.02	Nil	--	0.05	--
Acid value	mg KOH/g	11.0	0.24	0.35	<0.8	<0.50
Iodine value	--	101	104	-	-	-
Saponification value	--	194	190	-	--	--
Calorific value	MJ/kg	33	37.2	42	--	--
Cetane number	--	23	51.6	46	--	--

5.3.4. Characterization of karanja oil and karanja oil Methyl Ester

The fatty acid composition of karanja oil has been reported in Table 5.4 The measured values of properties of Karanja methyl esters are given in Table 5.5 and they have been compared with the others work. It is observed that the quality of biodiesel produced here are comparable with that of others and also with diesel fuel. It is also observed that the specific gravities of karanja methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these Karanja methyl ester is 37.12 MJ/kg, which is slightly lower as compared to diesel fuel (42.0 MJ/kg). The fuel properties of Karanja methyl esters were also within biodiesel specifications.

Table – 5.4: Properties of Karanja Oil

Properties	Karanja Oil
Acid Value (mg KOH/gm)	5.91
Saponification Value (mg KOH/gm)	191.5
Kinetic Viscosity at 38 ^{0}C mm^2/sec	41.8
Pour Point (^{0}C)	6
Flash Point (^{0}C)	232
Density (kg/l)	0.9326
Carbon Residue (wt%)	1.51
Ash (wt%)	0.014
Sulfur (wt%)	0.007
Properties	*Karanja Oil*
14:0	-----
16:0	1.3
18:0	0.5
18:1	60.9
18:2	31.2

Table – 5.5 Comparison of Properties of Karanja Methyl Esters with other work and diesel

Test Property	Karanja Methyl Ester	Raheman et al [21]	Naik et al [22]	Diesel
Acid Value (mg KOH/gm)	0.42	0.31	0.23	0.35
Saponification Value (mg KOH/gm)	187	-----	----	------
Iodine Value	91	-----	----	-----
Free Glycerin (wt%)	0.015	-----	102ppm	-----
Total Glycerin (wt%)	0.0797	-----	1867ppm	-----
Density (mg/lt)	0.867	0.876	-----	850
Conversion (%)	97.8	-----	------	-----
Flash Point (^{0}C)	183	187	174	68
Pour Point (^{0}C)	4	7	-----	-20
Cloud Point (^{0}C)	7	-----	-----	
Viscosity (c St) at 40 ^{0}C	4.657	9.6	4.33	2.6
Heating Value/Calorific value (MJ/kg)	37.12	36.12	-----	42
Cetane number	55.0	-----	57.6	-----
Ash Content (wt%)	0.098	0.01	-----	0.01
Aniline point (^{o}C)	128	----	-----	132
Carbon residue (%)	0.5445	0.24	-----	0.17

5.4. Conclusion

In the present work a comparison is made between Theoretical and Experimantal value of important chemical properties like acid value, saponification value and iodine value of non edible oil. A comparison is also made between different edible and non edible oil. . The theoretical values are in well agreement with their experimental values. The comparison of fuel properties are made between nonedible oil (mahua,karanja and jatropha) , methyl ester of non edible oil (mahua oil methyl ester, jatropha oil methyl ester and karanja oil methyl ester) with diesel.Thus this study suggests that the jatropha,mahua and karanja oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and/or transesterification.

But the production of biodiesel from edible oils is currently much more expensive than diesel fuels due to relatively high cost of edible oils. There is a need to explore non-edible oils as alternative feed stock for the production of biodiesel. Non-edible oil like jatropha, karanja and mahua are easily available in many parts of the world including India and it is cheaper compared to edible oils. The properties of bio diesel depend on the nature of the vegetable oil to be used for preparation of bio diesel and if the developed process is scaled up to commercial levels then excellent business opportunity will be offered by the biodiesel produced from non-edible oil.

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6. OPTIMIZATION OF ESTERIFICATION AND TRANSESTERIFICATION OF KARANJA OIL FOR PRODUCTION OF BIODIESEL

6.1. Introduction

Biodiesels (usually methyl esters) have continuously gained interests in many countries across the globe. Biodiesel is usually produced from vegetable oils by transesterification process. Transesterification refers to a base catalyzed chemical reaction involving oil/fat (triglycerides) and an alcohol (methanol/ ethanol) to yield fatty acid alkyl esters (i.e. biodiesel) and glycerol. The main factors affecting transesterification are the amount of alcohol and catalyst; reaction temperature and time; the contents of free fatty acids (FFAs) and water in oils [1]. Conversion of triglycerides into esters is complicated, if vegetable oils contain large amounts of FFA (>1% w/w) that will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction [1,2]. However, a two-step acid pretreatment of oil followed by base transesterification proved effective in producing the appropriate quality of biodiesel as per the ASTM specification [2–4]. In acid pretreatment, the vegetable oils are chemically treated with alcohol (methanol) in the presence of acid catalyst (H_2SO_4) for a specified time period and temperature just below the boiling point of the alcohol, to reduce the FFA content of oils to less than 1% for maximum biodiesel yield. Only a few attempts have been made in this regard and the pretreatment process parameters: methanol , catalyst , and time for some vegetable oils having a specified FFA content were optimized by using different optimization techniques and were found to be different for different vegetable oils [5–8]. Hence, a number of experiments have to be conducted for optimizing the pretreatment process parameters for vegetable oil when its FFA is different; these experiments require more chemicals, time and skilled job. Therefore, there is a need for development of a generalized model or technique, which can predict the optimized pretreatment process parameters for reduction of FFA content to around 1% w/w for any given vegetable oil.

One of the main problems related to the wide acceptance of biodiesel is its economic viability. In this sense, to extend the use of biodiesel, it is important to decrease the costs related to biodiesel production. Otherwise, the transesterification of fats and oils

provides a costly fuel compared to diesel fuel. In fact, it is reported that approximately 70-95% of the final cost of biodiesel arises from the cost of the raw materials [9-10]. So, to decrease the final cost of biodiesel, it is important to select inexpensive or low-cost raw materials, that is, used frying vegetable oil [11-14].

On the other hand, time-consuming and costly laboratory tests are required to conduct the optimization of the parameters involved in the transesterification of the oils or fats, at each working condition. For this reason, it is of interest to implement a simulation process to accurately predict the biodiesel yield evolution while varying the initial condition values, thus, substituting part of the laboratory tests. However, the optimization of the chemical reaction that is required to produce biodiesel, called transesterification, is a costly and time-consuming process that needs expensive reactants and laboratory equipments.

An artificial neural network (ANN) is an abstract model of a human neural system that contains a collection of neurons communicating with each other via axon connections. This technique is capable of dealing with nonlinear problems where the network is trained to predict and generalize with very high precession. Since the first fundamental modeling of neural nets was proposed in terms of a computational model provided in [15]. ANNs have shown their suitability in diverse fields such as control, robotics, pattern recognition, forecasting, medicine, power systems, manufacturing, optimization, signal processing, and social and psychological sciences [16-17].The study of biodiesel production from Jatropha oil has been conducted by several researchers, but with differing production processes, optimum conditions, and methyl ester yields [18-20]. Crude *Jatropha curcas* oil was used as feedstock for biodiesel production by alkali-catalyzed methanolysis. The reaction in the presence of NaOH as catalyst was carried out to investigate the optimum conditions and to study the effects of variables on the reaction [21].

The aim of this study is to determine whether the ANN can accurately simulate the performance of the esterification and transesterification reaction in order to obtain biodiesel from karanja oil, under different working conditions. Also, another objective is to provide a tool to assist decision making during the experimental process of biodiesel production from Karanja oil.

In the first part of this experimentation the study is carried out with important process variables for optimization of esterification and transesterification reaction to achieve maximum bio diesel production. The important process variables for esterification such as concentration of acid catalyst, alcohol/oil ratio, reaction time, temperature, and % of excess alcohol; and for transesterification; concentration of alkali catalyst, alcohol/oil ratio, reaction time, temperature, % of excess alcohol are optimized.

In the next stage of this research work, an artificial neural network (ANN) based model for simulation of biodiesel production through the esterification and transesterification of Karanja oil has been developed. Afterwards, the model is validated with sets of experimental data obtained from the laboratory experiment and that were not used during the training procedure. The results of simulation experiment are found to be similar to those obtained with the help of the tests required to perform the esterification and transesterification process in a laboratory, thus, indicating that the prediction of model of biodiesel yield function is in well match with the real process. It can be conclude that artificial neural networks can be used to predict the biodiesel yield from Karanja oil.

6.2. Result and Discussion

6.2.1. Optimization of the esterification and Transesterification Process by Laboratory Tests

6.2.1.1 Esterification

Esterification result shows that the concentration of acid catalyst is 4 % (H_2SO_4), alcohol/oil ratio = 0.33%v/v, reaction time = 1 hr , temperature = 65^0C for maximum esterification. It is found that the effect of temperature on acid value is an important factor for esterification reaction**.** Acid catalyst is a better choice for esterification reaction because the reduction of Free Fatty Acid is very fast and requires less time. (**Figure 6.1 - 6.4)**

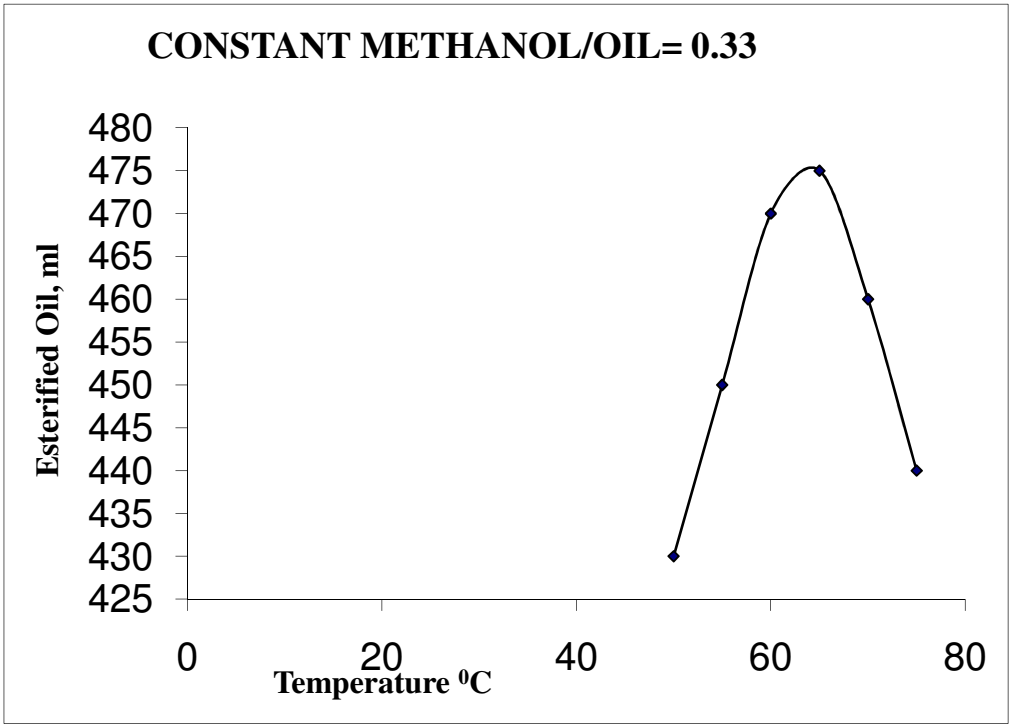

Figure 6.1 Effect of temperature (^{0} C) on esterified oil (ml) for constant methanol/oil ratio 0.33% v/v, acid catalyst = 4 %(H2SO4) and reaction time = 1 hr.

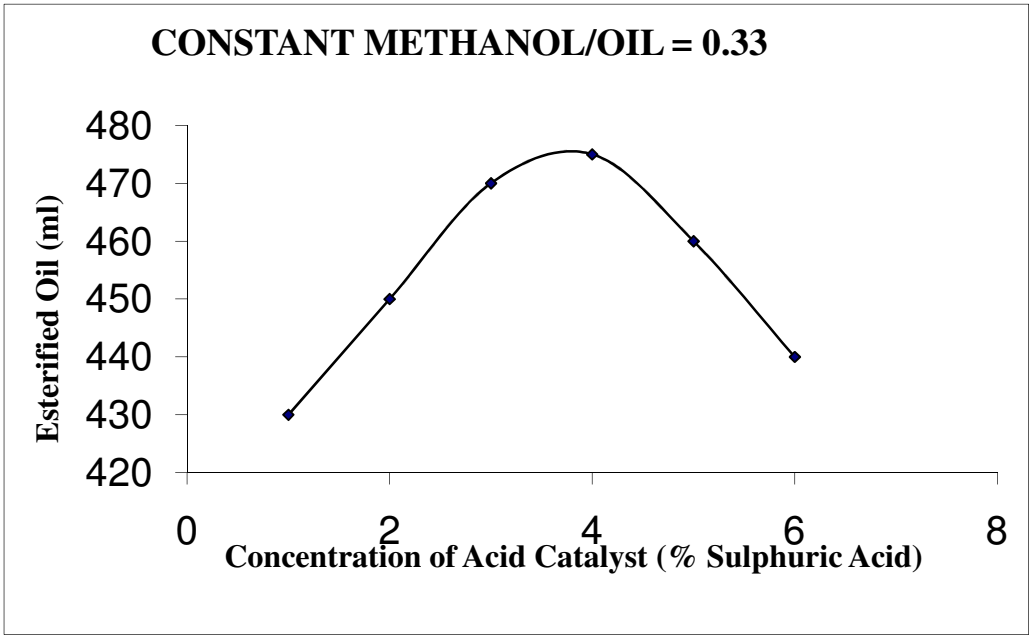

Figure 6.2 Effect of % of acid catalyst and esterified oil (ml) for constant methanol/oil ratio 0.33% v/v, temperature (65^0C) and reaction time = 1 hr

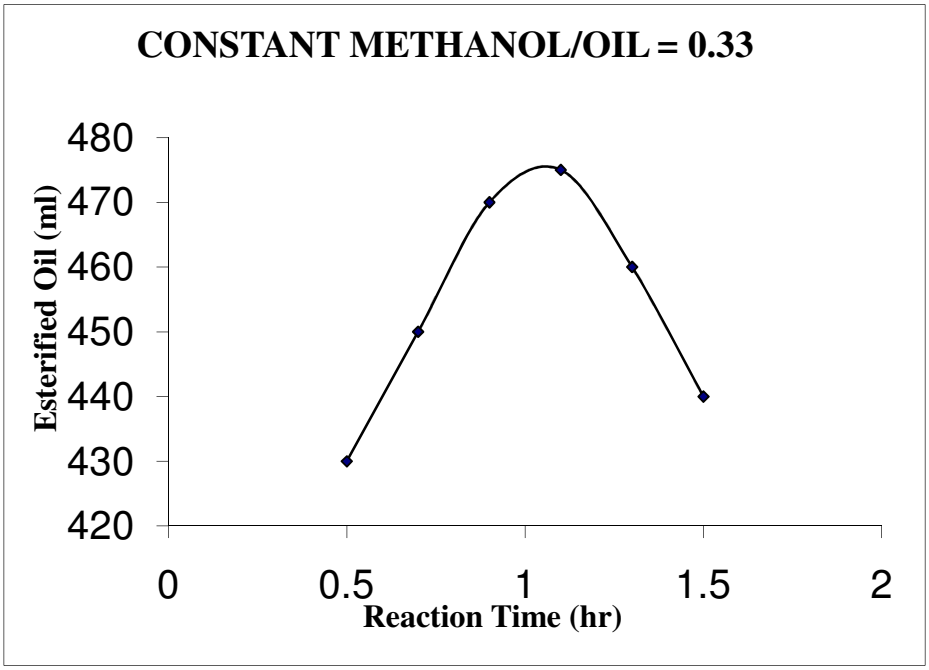

Figure 6.3 Effect of reaction time (hr) on esterified oil (ml) for constant methanol/oil ratio 0.33% v/v temperature (65^0C) and acid catalyst = 4%(H_2SO_4).

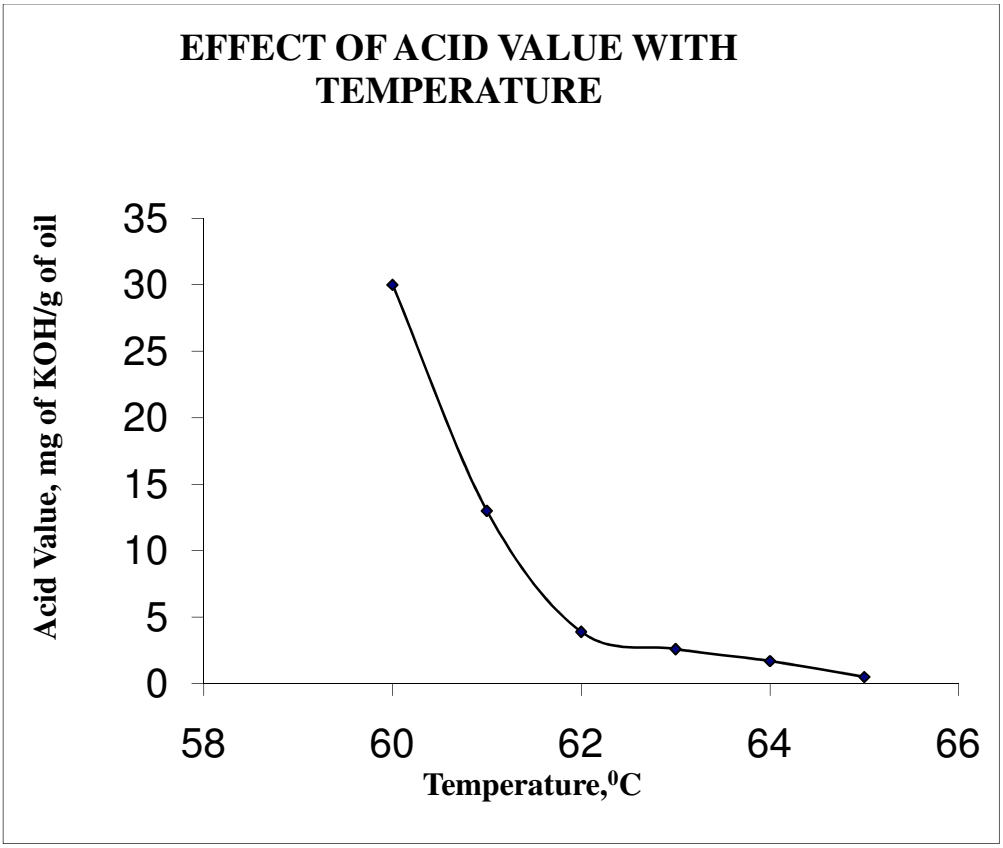

Figure 6. 4 Effect of Temperature on Acid value for constant methanol/oil ratio 0.33% v/v ,Reaction time = 1 hr and acid catalyst = 4%(H_2SO_4)

6.2.1.2.Transesterification

For maximum bio diesel production the transesterfication reaction shows that the concentration of alkali catalyst is 8 % Sodium Methoxide, alcohol/oil ratio = 0.33%v/v, reaction time = 1 hr , temperature = 65^0C and excess alcohol = 150%v/v. For tranesterification alkali catalyst is a better choice because the reaction is very fast and requires less amount of catalyst. **(Figure 6. 5- 6.8)**

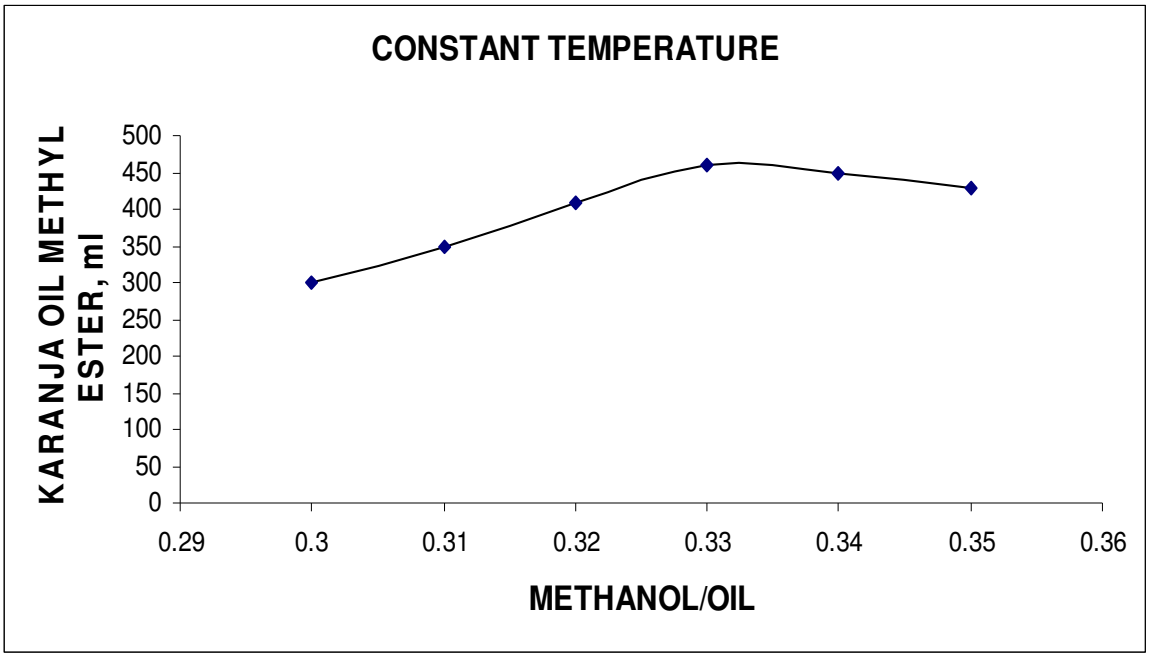

Figure 6.5 Effect of methanol/oil ratio on KOME yield for constant temperature (65^0C) Reaction time = 1 hr and alkali catalyst = 0.8 wt % sodium methoxide, excess alcohol = 150 %

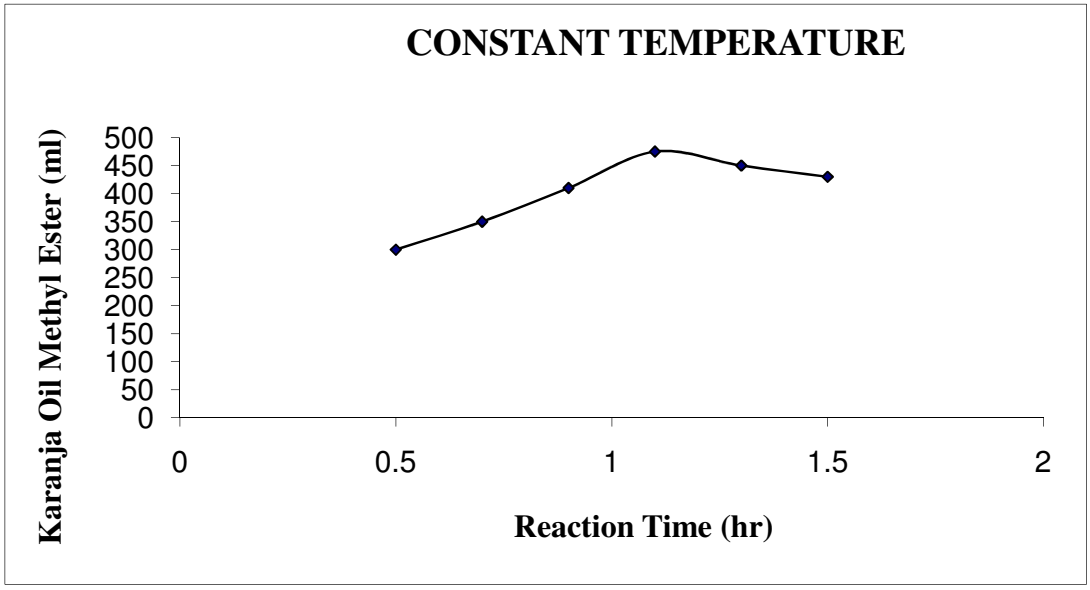

Figure 6.6 Effect of reaction time on KOME yield for constant temperature (65^0C)methanol/oil ratio 0.33% v/v , alkali catalyst = 0.8 wt % sodium methoxide, excess alcohol = 150 %

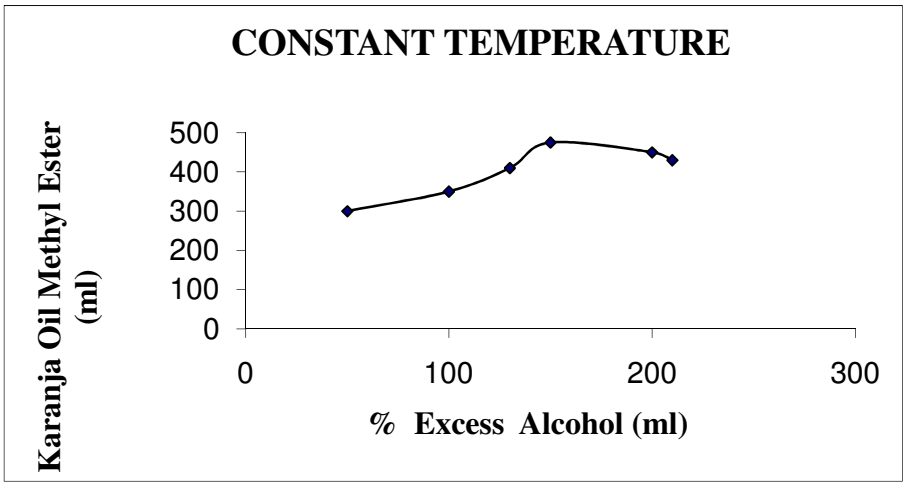

Figure 6.7 Effect of % of excess alcohol on KOME yield for constant temperature (65^0C) methanol/oil ratio 0.33% v/v, alkali catalyst = 0.8 wt % sodium methoxide, and reaction time = 1 hr.

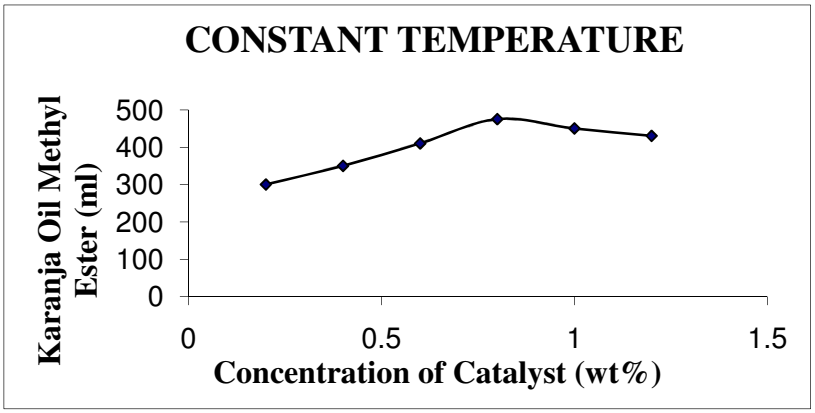

Figure 6.8 Effect of concentration of alkali catalyst and KOME for constant temperature (65^0C) methanol/oil ratio 0.33% v/v, excess alcohol = 150 % and Reaction time = 1 hr

In case of Figure 6.5, Effect of methanol/oil ratio on KOME yield for constant temperature , Reaction time and alkali catalyst is given. In this case product yield will increase until equilibrium so product yield is reduced beyond 0.33 methanol/oil ratio.In case of Figure 6.6 Effect of reaction time on KOME yield for constant temperature ,methanol/oil ratio and alkali catalyst .In this case product yield is varied with temperature but not with methanol/oil ratio.In case of Figure 6.7 Effect of % of excess alcohol on KOME yield for constant temperature, methanol/oil ratio and alkali catalyst and reaction time is studied. In this case product yield is varied with % of excess alcohol but not with methanol/oil ratio

So as a whole trend is different in different condition. Effect of reaction time on KOME yield for constant temperature ,methanol/oil ratio and alkali catalyst .In this case product yield is varied with temperature but not with methanol/oil ratio

6.2.2. Optimization of Esterification and transesterification process parameters for the production of biodiesel from Karanja oil using ANN approach

As the ANN built for this research was a multilayer perceptron network, with three layers of neurons. In case of esterification ,the number of input layer neurons ($x1$, $x2$ and $x3$) and output layer neurons (estimated Esterified Oil) is fixed (see Materials and Methods), while the number of hidden neurons is determined by a heuristic procedure. In case of trans esterification ,the number of input layer neurons ($x1$, $x2$, $x3$ and $x4$) and output layer neurons (estimated biodiesel yield) is fixed (see Materials and Methods), while the number of hidden neurons is determined by a heuristic procedure. This method revealed that the optimum number of hidden neurons is 11 for esterification and 21 for transesterification. Results of this esterification and transesterification process are plotted in

Figure 6.9 and 6.10. MSE is a network performance function. It measures the network's performance according to the mean of squared errors [22]

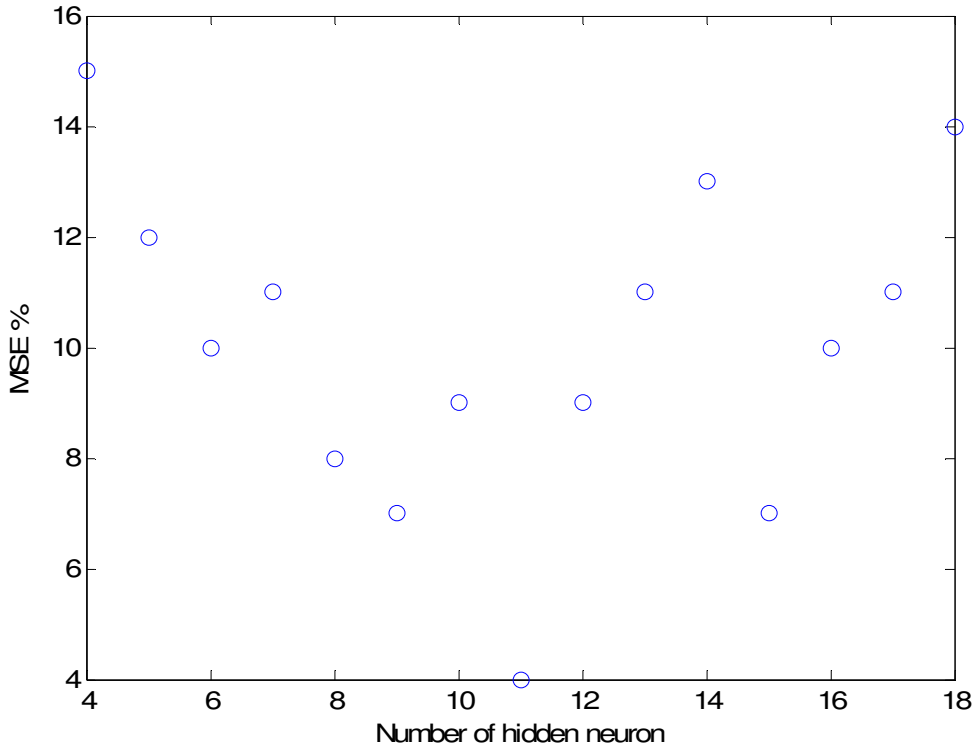

Figure 6.9 Heuristic determination of the optimum number of neurons of he hidden layer in case of esterification

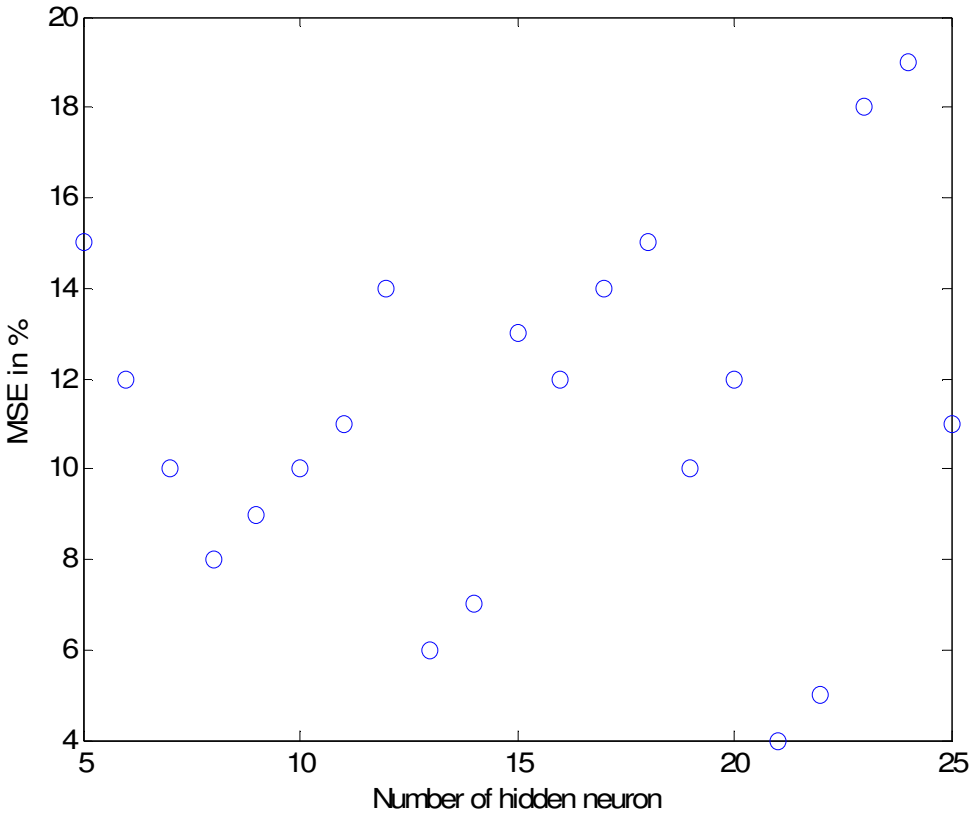

Figure 6.10 Heuristic determination of the optimum number of neurons of he hidden layer in case of Transesterification.

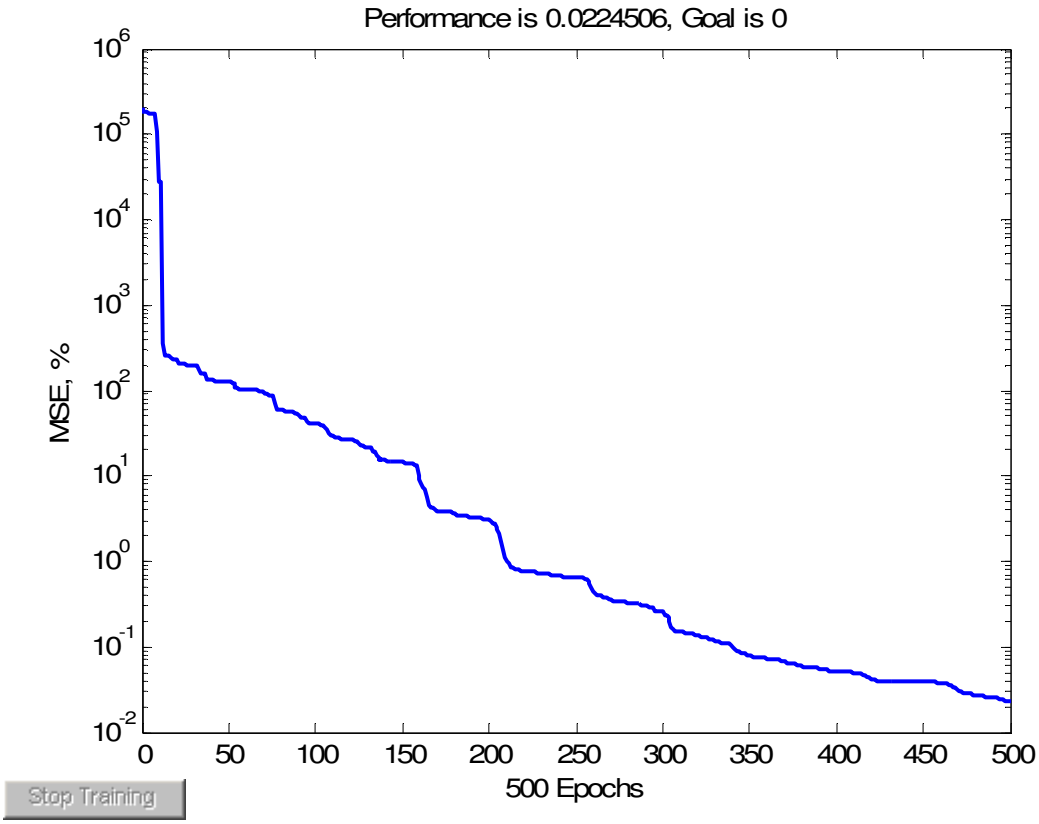

Figure 6.11 Training with back propagation method. Calculation of the weights during the convergency of the neural network in case of esterification

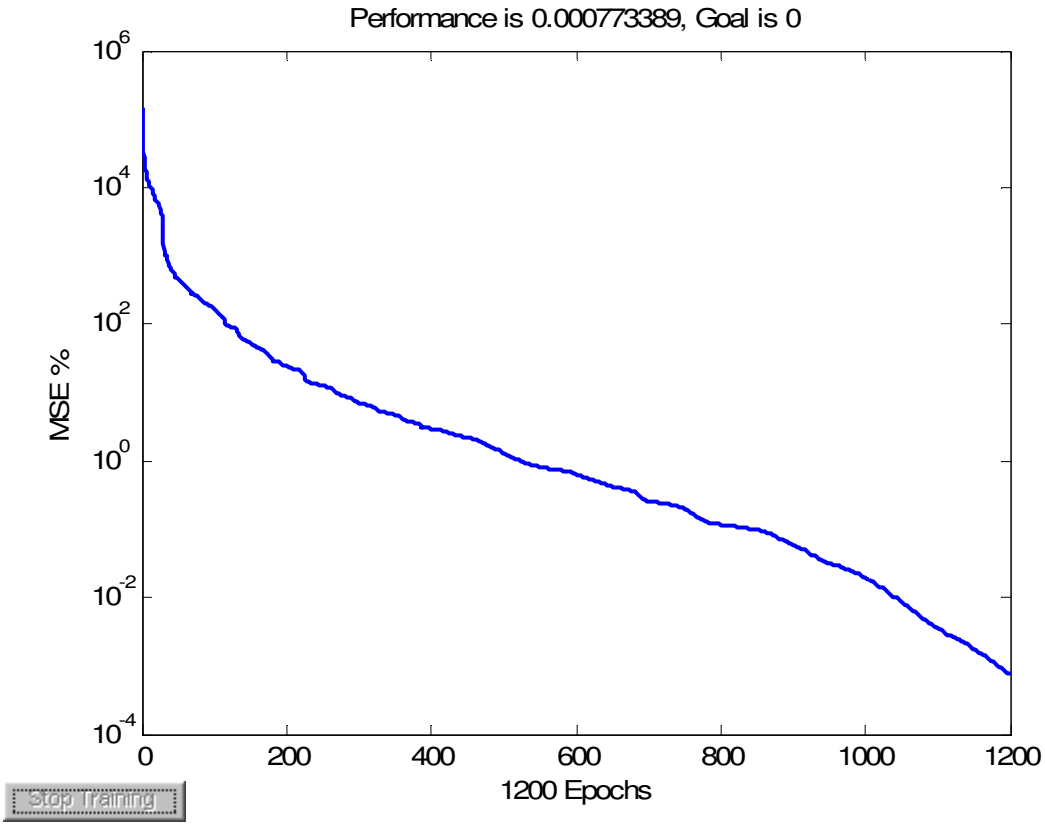

Figure 6.12. Training with back propagation method. Calculation of the weights during the convergency of the neural network (in case of Transesterification)

Figure 6.11 and 6.12 shows an example of the first stage of the process. It can be seen that the initially high mean squared error descended quickly to a small value. The process ended when the validation subset error reached the desired low value.

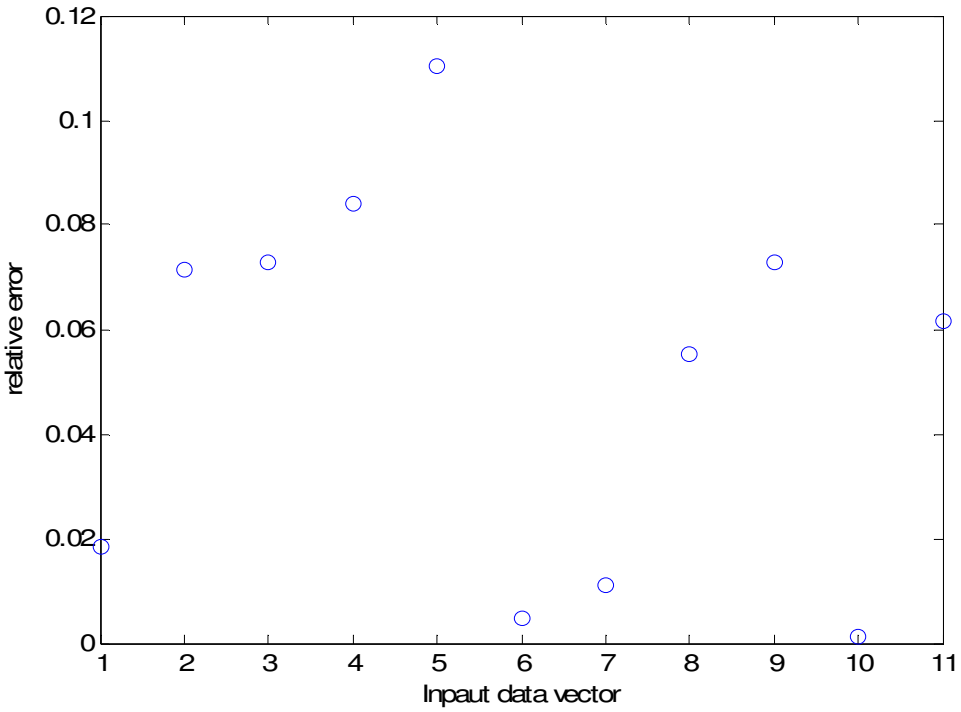

Figure 6.13 Relative error of the network validation subset (Esterification)

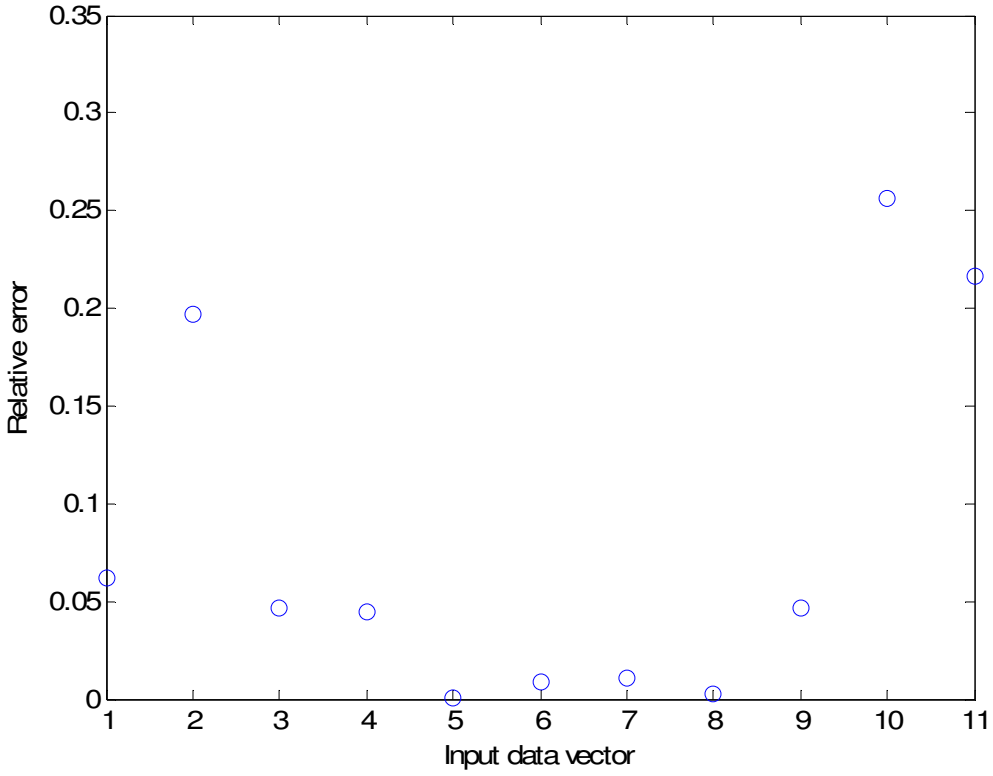

Figure 6.14. Relative error of the network validation subset (Transesterification)

Figure 6.13 and 6.14 shows the relative error of several patterns according to this subset. To perform the modeling technique, a set of input-output data was required. From the available data, some of them are used for training the model, and the remaining data (still a high amount of data, called the testing set) were employed afterward to validate the network training and to check the prediction power of the present proposal. According to this, a set of samples is used for training the neural network.

For these samples, In case of esterification the reaction temperature ($x1$) varied from 50^0C to 65^0C , % of catalyst ($x2$) varied from 1 to 4 and the reaction time ($x3$) from 30 to 90 minutes Similarly , In case of esterification the methanol to oil ratio ($x1$) varied from 0.3 to 0.35 , the reaction time ($x2$) from 30 to 90 minutes ,excess alcohol ($x3$) 50 to 210 % and % of catalyst ($x4$) varied from 0.2 to 1.2 .

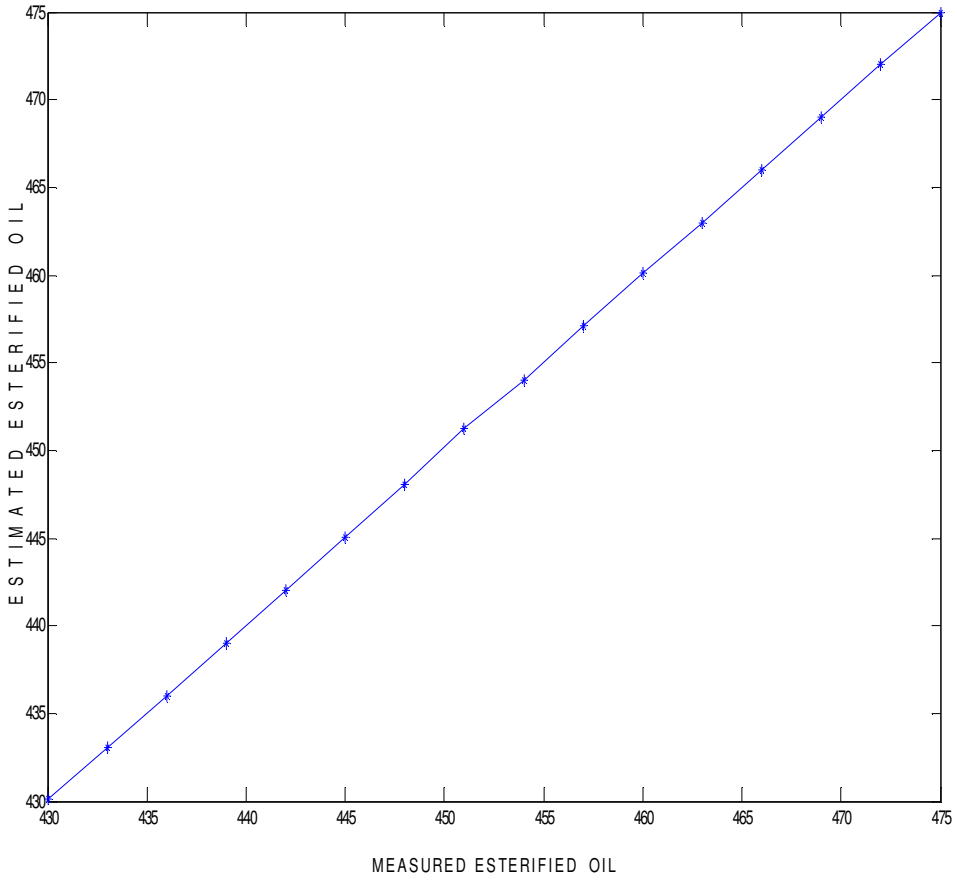

Figure 6.15 Comparison of actual and predicted Esterified oil by ANN.

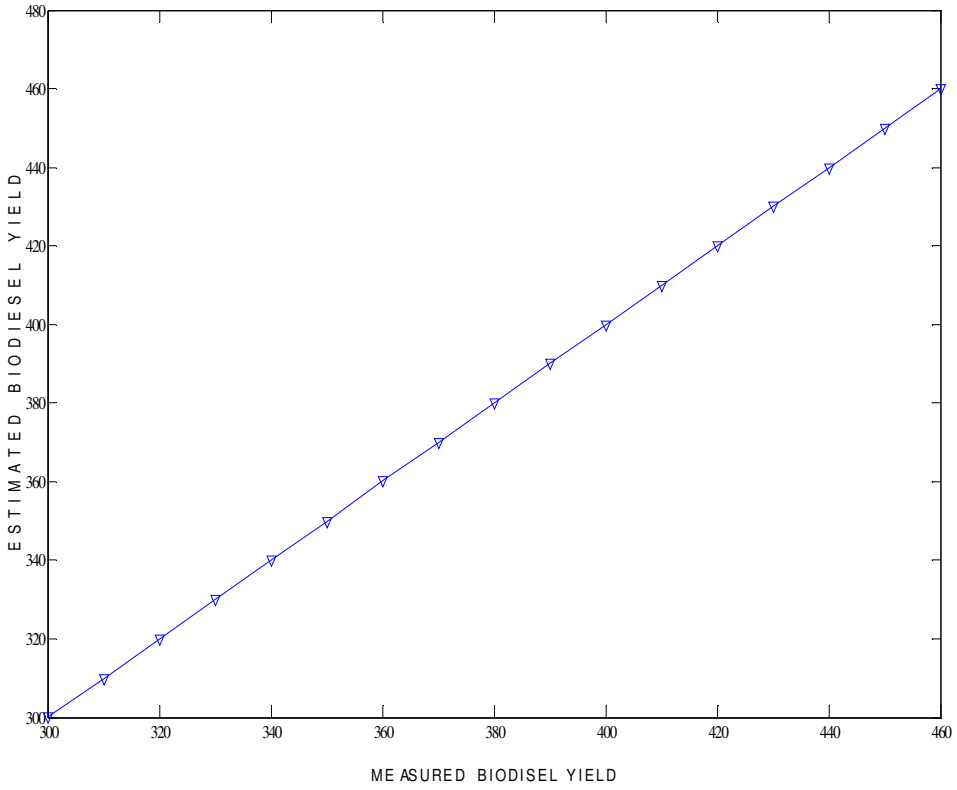

Figure 6.16 Comparison of actual and predicted Biodiesel yield by ANN.

Once the ANN is trained and validated, the proposed ANN successfully predicted a set of samples picked at random from the region defined for the testing set. The training data and predicted ANN values between Measured and Estimated values of experimental data given for esterification and transesterification are presented in **Fig. 6.15 and 6.16** respectively. The results indicate a good agreement between Measured and Estimated values of esterified oil and biodiesel. It is worth noticing, in general, that the predictions obtained from the ANN technique are very good for all situations during biodiesel production, thus, demonstrating the ANN's modeling capabilities.

6.2.3. Conclusions

This study suggests that the karanja oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and transesterification. The Free Fatty acid of crude Karanja oil was reduced to less than 1% by using acid catalyst. The high Free Fatty

acid (30%) of crude karanja oil was reduced to less than 1% by using acid catalyst .The results show that optimum conditions for esterification are 4 %H_2SO_4, 0.33%v/v alcohol/oil ratio, 1 hr reaction time and temperature of 65 ^{0}C. For maximum (95%) bio diesel production the transesterification reaction shows that the concentration of alkali catalyst is 8 % Sodium Methoxide, 0.33%v/v alcohol/oil ratio, 1 hr reaction time, 65^{0}C temperature and excess alcohol 150%v/v.

Again the results demonstrate that the ANN represents a strong alternative to the extensive laboratory testing needed to find out the optimum parameters to produce biodiesel from karanja oil. In fact, simulated and experimental values are almost the same. This methodology has proven to be capable of modeling the production of biodiesel from karanja oil, which is a process with a high nonlinear behavior. In the present work, however, the available set of experimental data makes possible the establishment of a comparison between the experimental and estimated data (from the expert system), leading to a better understanding of the influence of the interactions between the reaction parameters, thus, helping to improve the esterification and trans esterification process to produce biodiesel from karanja oil and, in summary, reducing costs and long time-consuming laboratory tests.

6.4. References

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7. PERFORMANCE AND EMISSION ANALYSIS OF PREHEATED AND BLENDED KARANJA OIL AS FUEL IN C.I ENGINE

7.1. Introduction

In a developing country like India major concentration has been focused on non-edible oils as the fuel alternative to diesel because edible vegetable oils have their use in our day-to-day life.

As India is deficient in edible oils, non-edible oil is the main choice for producing bio diesel. In remote areas, different types of non edible oils like karanja, neem, Jatropha, and Mahua are cultivated locally but it may not be possible to convert into biodiesel. Out of all the above prospective biodiesel yielding sources, *Pongamia pinnata* or Karanj stands at the top because most of the states of India are tribal where it is found abundantly.

Karanja is one such forest-based tree-borne non-edible oil with a production potential of 135,000 million tones [1]. Karanja oil has been widely tested for insecticidal and bactericidal activity. In south part of the Indian peninsula the karanja oil/cake are also used same like neem oil and neem cake. The oil expelled from the seeds is also burned during the festival of lighting to purify the environment. All these applications are at local or regional level and 94% of the oil from plant is still underutilized. The oil is used by common people due to its low cost and easy availability. The fatty acid composition of karanja oil has been reported in **Table – 7.1**[2]

Table – 7.1 : Different fatty acids present of karanja oil [2]

Fatty acid (common name)	Systematic name	Formula	Structure	wt%
Palmitic	Hexadecanoic	C16H32O2	16:0	10.6
Stearic	Octadecanoic	C18H36O2	18:0	6.8
Oleic	cis-9-octadecenoic	C18H34O2	18:1	49.4
Linoleic	cis-9, cis-12-octadecadienoic	C18H32O2	18:2	19.0
Arachidic	Eicosanoic	C20H40O2	20:0	4.1
Gadoleic	11-eicosenoic	C20H38O2	20:1	2.4
Behenic	Docosanoic	C22H44O2	22:0	5.3
Lignoceric	Tetracosanoic	C24H48O2	24.0	2.4

The non-edible oil is being used in the soap and pharmaceutical industries, but due to the dark colour and odour of karanja oil, it is less preferable compared to other non-edible oil species. In rural areas, where grid power is not available, non edible oils can play a vital role for irrigation and electrification. Vegetable oils can be produced even on a small scale for on-farm utilization to run tractors, pumps and small engines for power generation/irrigation. Suitability of vegetable oils as fuels for diesel engines depends on their physical, chemical and combustion characteristics as well as the type of engine used and operating conditions [2-3]. It has been observed that biodiesel can effectively be used as diesel fuel substitute in exiting diesel engine without any engine modification [4]. Biodiesel can be used as an alternative to diesel in a compression ignition engine without any engine modifications[5]. Biodiesel produces lower smoke opacity (up to 60%), and higher brake specific fuel consumption (BSFC) (up to 11%) compared to diesel fuel[6].

Vegetable oils can also be used directly or blended with diesel to operate compression ignition engines. Use of blends of vegetable oils with diesel has been experimented successfully by various researchers in several countries [7-11].It can be used directly in the engine without any previous treatment with the required engine modification or in the form of biodiesel. The later needs investment and high skill for its preparation from vegetable oils and adds extra cost of processing because of the transesterification reaction involving chemical and process heat inputs. In these remote areas, different types of vegetable oils are grown / produced locally but it may not be possible to chemically process them. In the present study, keeping these facts in mind, a set of engine experiments were conducted using karanja oil on a engine. Heating and blending of vegetable oil were used to lower the viscosity of Karanja oil in order to eliminate various operational difficulties.

In this present work the high viscocity karanja oil is blended with diesel in various proportions. Diesel, karanja oil fuel blends (10% and 20%) and preheated karanja vegetable oil (At 100^0C and 120^0C) are used to conduct short-term engine performance and emission tests at varying loads (0%, 20%, 40%, 60%, 80%, and 100%).The performance and emission characteristics of a single cylinder, 5 hp, four stroke, constant speed, water cooled, direct injection diesel engine is used in stationary condition. Tests are carried out

for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emission of CO, CO_2, HC and NO_x gases in exhaust. The performance of preheated and blended (lower blend concentrations) Karanja oil are found to be very close to mineral diesel. The performance of preheated karanja vegetable oil is found to be slightly inferior in efficiency due to low heating value. It can perform well in the unmodified engine for a long period of operation without any ignition problem. People of rural and undeveloped areas can use this oil for their agricultural engines without depending on market and without modification of whole engine, at the same time they can reduce the requirement of diesel fuel from outside market.

7.2 Extraction of karanja oil

For extraction of oil from Kernel of Karanja two methods have been identified. They are the chemical extraction with n-hexane and mechanical extraction method in two stages using screw type of expellers. In the present study, the chemical extraction process gave the oil content about 32 to 33% from the kernel. In the two stages expellers the oil extracted were only 20 to 24%.

7.3. Characterization of Karanja oil

Various properties of crude karanja oil and it's methyl ester, such as density, kinematic viscosity, free fatty acid, moisture content flash point, fire point, ash content estimation, carbon residue estimation, specific gravity measurement, pour point, iodine number, saponification number, acid value, aniline point are determined as per ASTM standard (Table 4.1).

7.4. Result and Discussion

7.4.1 Effect of blending Karanja oil on Physical, chemical and thermal Properties

The various properties of diesel blended with karanja oil are analyzed as per the ASTM standard and results are shown in **Table.7.3** The viscosity of blended karanja oil from 10% to 20 % are in the range of ASTM limits of diesel fuel use in diesel engines i.e. 6 and hence gone for engine performance testing .The energy content of Karanja oil–diesel blended fuels decreases as Karanja oil is added to the pure diesel fuel. The flashpoint temperature of Karanja oil is higher than the pure diesel fuel. The high flash point

temperature of Karanja oil is a beneficial safety feature, as the fuel can be safely stored and transported at the room temperature.

Table.7.2 - Properties of oil blends

Sl.No.	Types of oil blends	Sp.gravity	Calorific value (KJ/kg)	Flash point (^{o}C)	Fire point (^{o}C)
1	100%oil	0.904	35000	147	158
2	90%oil+10%diesel	0.89	35900	138	147
3	80%oil+20%diesel	0.882	36700	132	141
4	70%oil+30%diesel	0.875	37800	124	135
5	60%oil+40%diesel	0.866	38600	114	125
6	50%oil+50%diesel	0.858	39400	107	116
7	40%oil+60%diesel	0.850	40800	92	105
8	30%oil+70%diesel	0.842	41600	83	94
9	20%oil+80%diesel	0.838	42210	72	81
10	10%oil+90%diesel	0.834	42500	68	75
11	100%diesel	0.828	43000	55	64
12	Preheated oil at 100^{0}c	0.89	35000	147	158
13	Preheated oil at 110^{0}c	0.874	35000	147	158
14	Preheated oil at 120^{0}c	0.855	35000	147	158

7.4.2 Effect of temperature on viscosity in Karanja oil

From the properties studies of Karanja oil it has been observed that the viscosity is not acceptable for the diesel engines. In order to make the karanja vegetable oil suitable for diesel engine, the viscosity is required to be reduced. Therefore an effort has been given to reduce the viscosity by heating the Karanja vegetable oil in a range of 40^{o}C to 120^{o}C.The results are shown in **Figure 7.1**. The viscosity decreases considerably as the temperature increases and are close to diesel engine operation at about 120^{0}C.After studying this experiment has been conducted on preheated oil from 100^{0}C to 120^{0}c for engine testing.

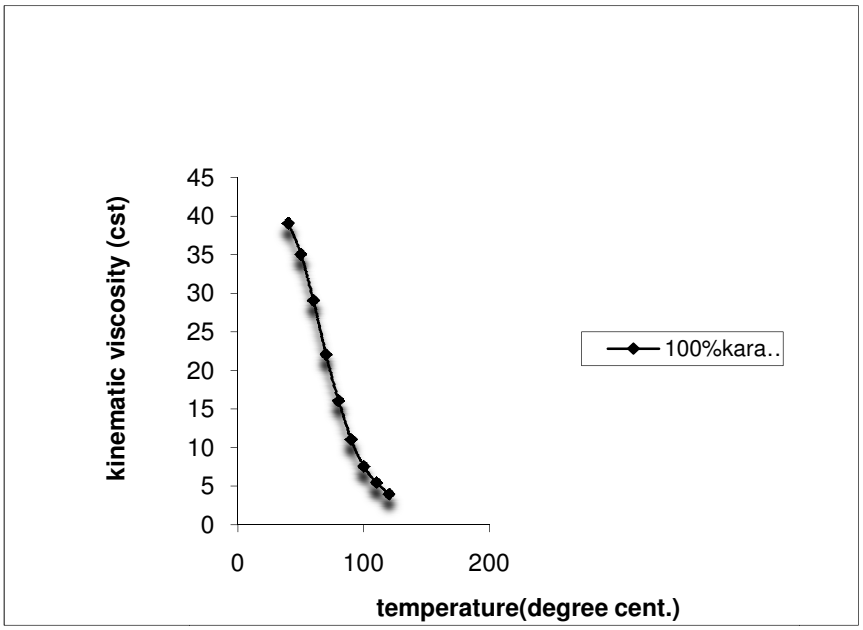

Figure 7.1 Effect of temperature on viscosity of Karanja oil

7.5 Engine test results and discussion

7.5.1 Effect of brake power on brake specific fuel consumption

The specific fuel consumption of diesel blends of Karanja oil and preheated karanja oil up to (120^{o}C) at varying break loads shown in the **Figure 7.2** .Engine works, giving better performance for 20 % oil. The *bsfc* of diesel engine depends on the relationship among the amount of fuel injected; fuel density, viscosity and heating value 8-11[5-8]. More blended fuels are needed to produce the same amount of energy produced by the pure diesel fuel due to the low heating value of Karanja oil. It is also shown that there is decrease in bsfc values at high engine loads under all operating modes. It is observed that specific fuel consumption of preheated karanja oil, blended oil is higher than diesel at different percentage of loads. The higher density of the Karanja oil has led to more discharge of the fuel for the same displacement of the plunger in the fuel injection pump [12]. This is probably due to the low volatility and higher viscosity of the preheated karanja oil, karanja oil and its blends [13] which affect mixture formation of the fuel and leads to incomplete combustion.

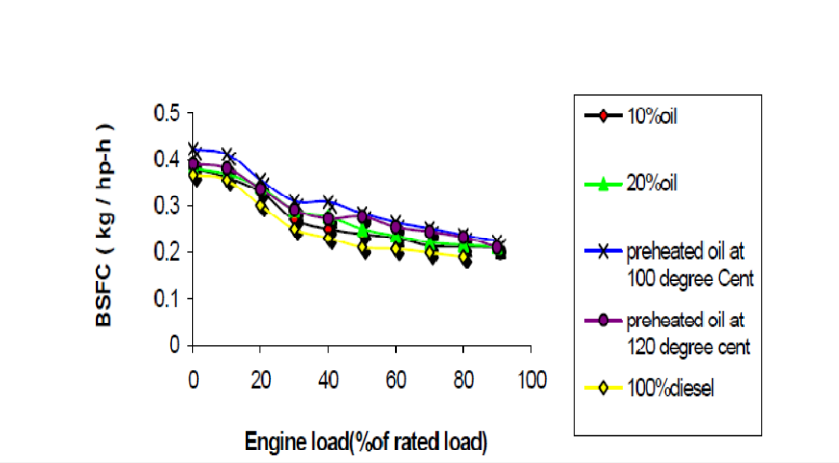

Figure 7.2 Effect of percentage of brake power on specific fuel consumption for diesel, various blends and preheated oil.

7.5.2 Effect of break power on brake thermal efficiency

The variation of break thermal efficiency of the engine with various fuel i.e. diesel, blended diesel with karanja oil and preheated karanja oil is shown in **Figure 7.3.** In all the cases, with increase in engine load the thermal efficiency increases. The brake thermal efficiency of the karanja oil and its blends are lower than that of diesel throughout the entire range. The drop in thermal efficiency with increase in proportion of vegetable oil must be attributed to the poor combustion characteristics of the vegetable oils due to their high viscosity and poor volatility.

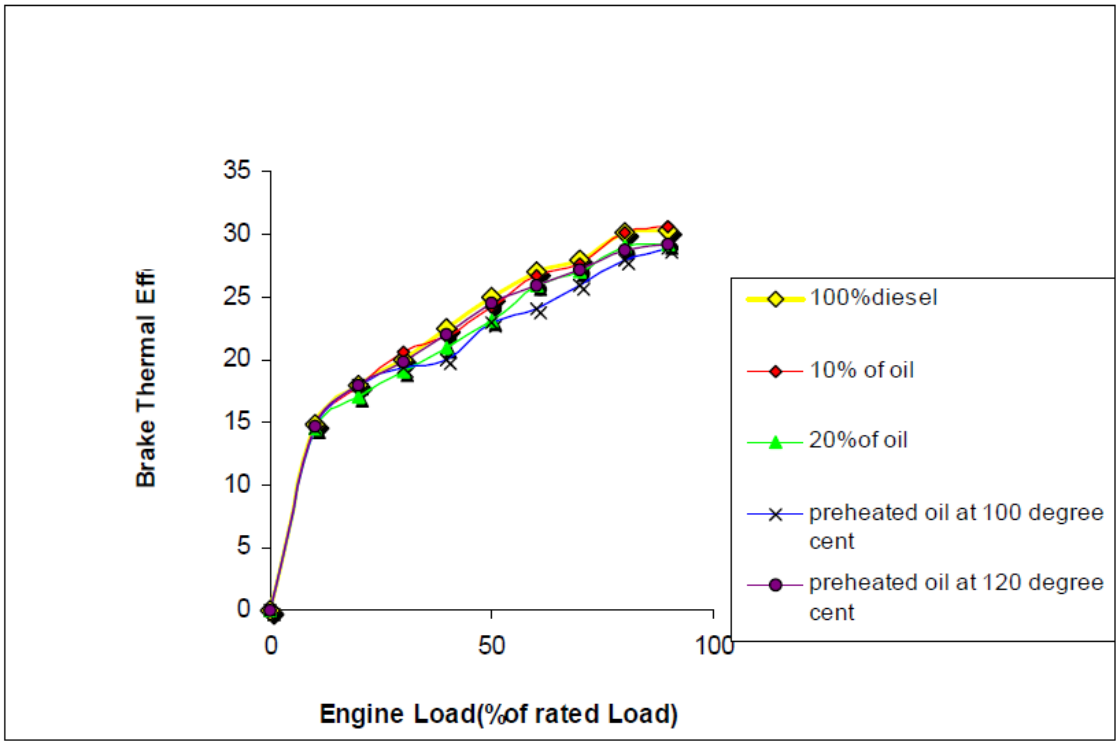

Figure 7.3 Variation of brake thermal efficiency with percentage of engine load for diesel, preheated oil and various blends.

7.5.3 Effect of break power on exhaust gas temperature

Figure 7.4 shows the variation of exhaust gas temperature with different percentage of load of the engine .The result shows that the exhaust temperature increases with increase in engine load in all the cases. The exhaust gas temperature of preheated oil and blends are lower than pure diesel.. This is due to the poor combustion characteristics of the karanja oil because of its high viscosity. Exhaust gas temperature is less for 20 % oil blend.

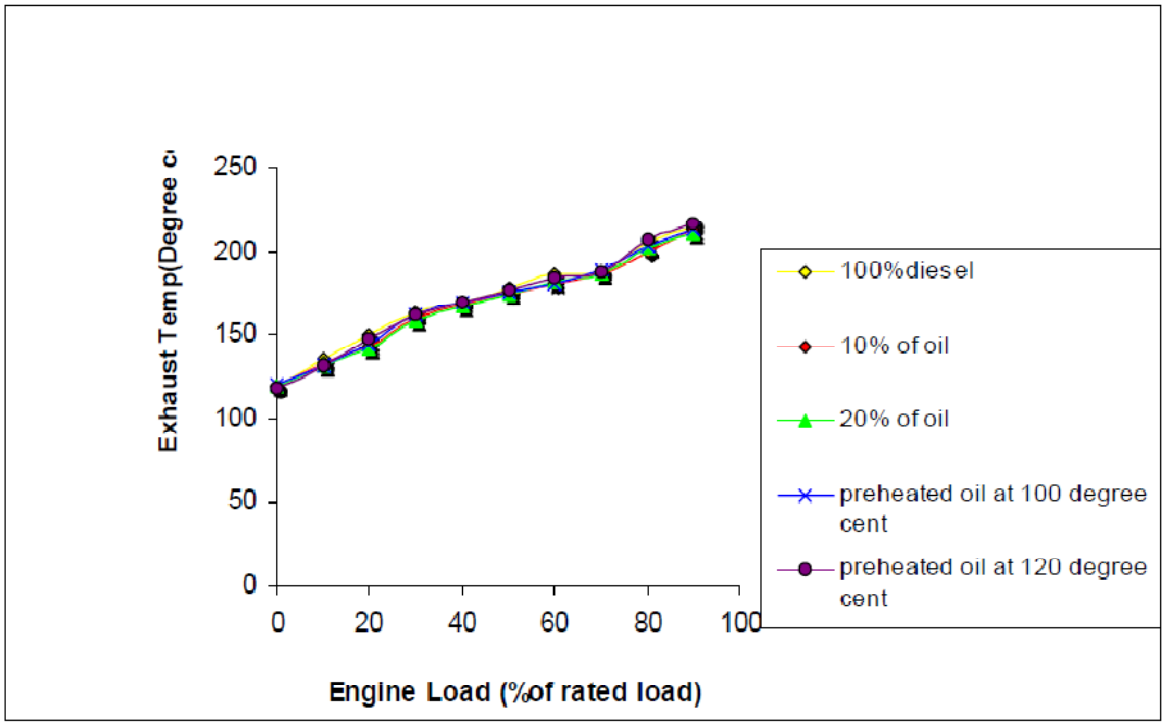

Figure 7.4 Effect of load on exhaust gas temperature for diesel, Pre heated oil and various blends.

7.5.4 Effect of break power on engine emission

The emission results of Diesel, preheated karanja oil, karanja oil and its blends are given in **Figures 7.5–7.8**. The CO, CO_2, HC and NO_X emissions of preheated karanja oil is higher than diesel and blends. Emission level of Pre heated oil at 120 ^oC is lower than emission level of preheated oil at 100^oC. It is also observed that in most of the cases, emission goes on increasing with increase in engine load.

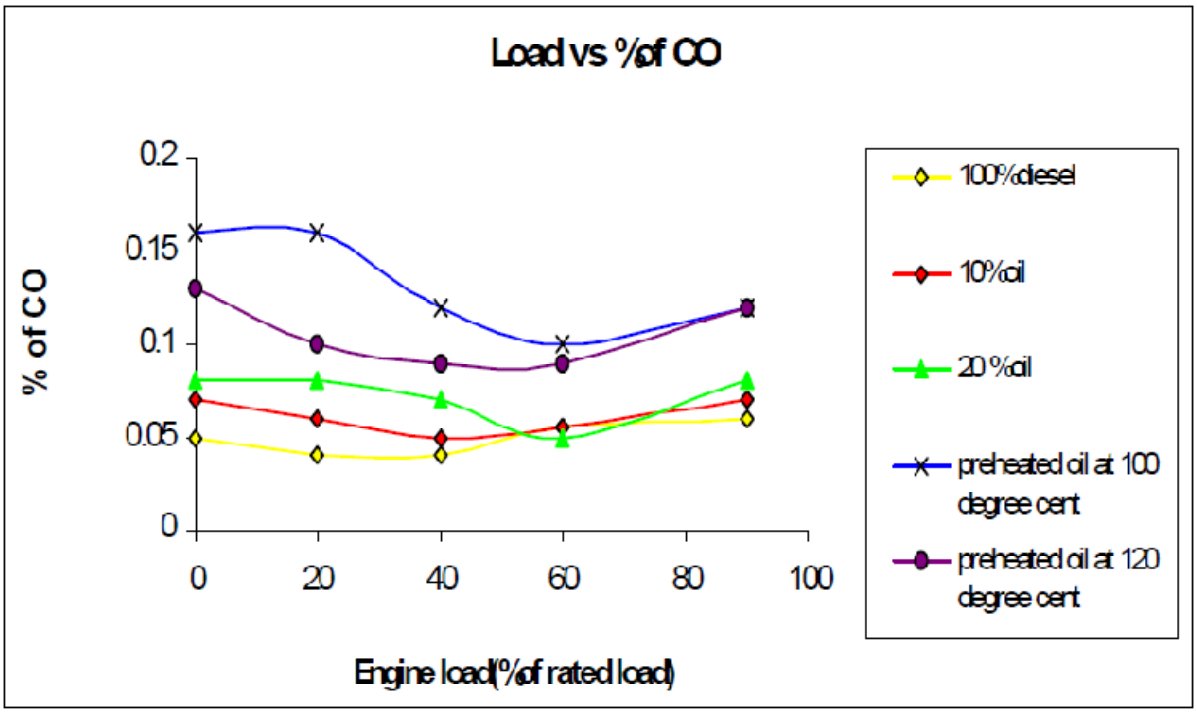

Figure 7.5 Carbon monoxide emissions vs. % engine load for the tested fuels.

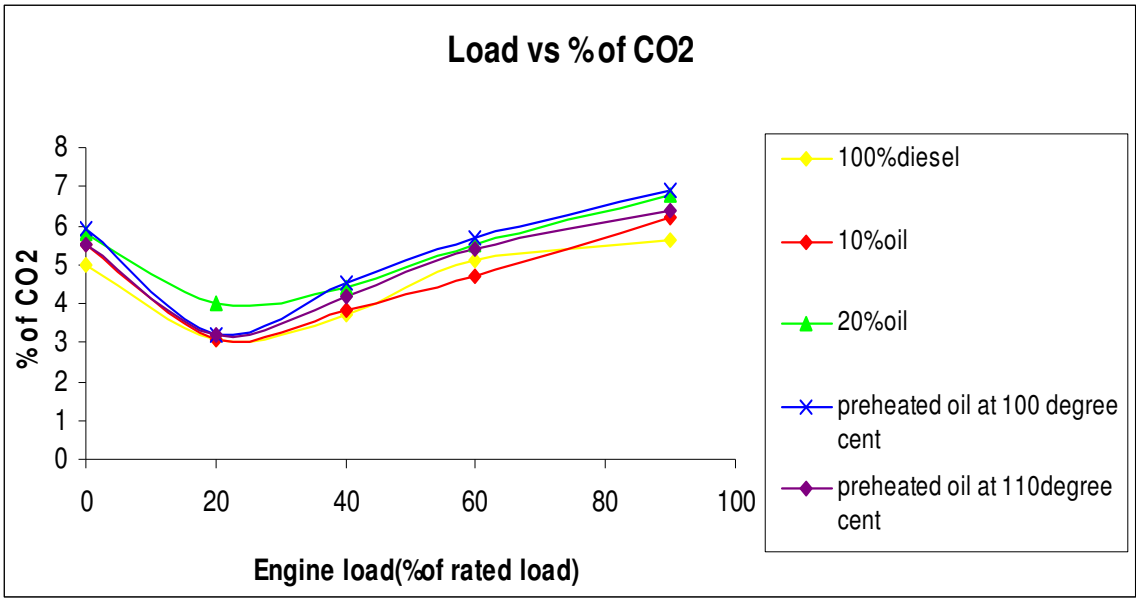

Figure 7.6 Carbon dioxide emissions vs. % engine load for the tested fuels.

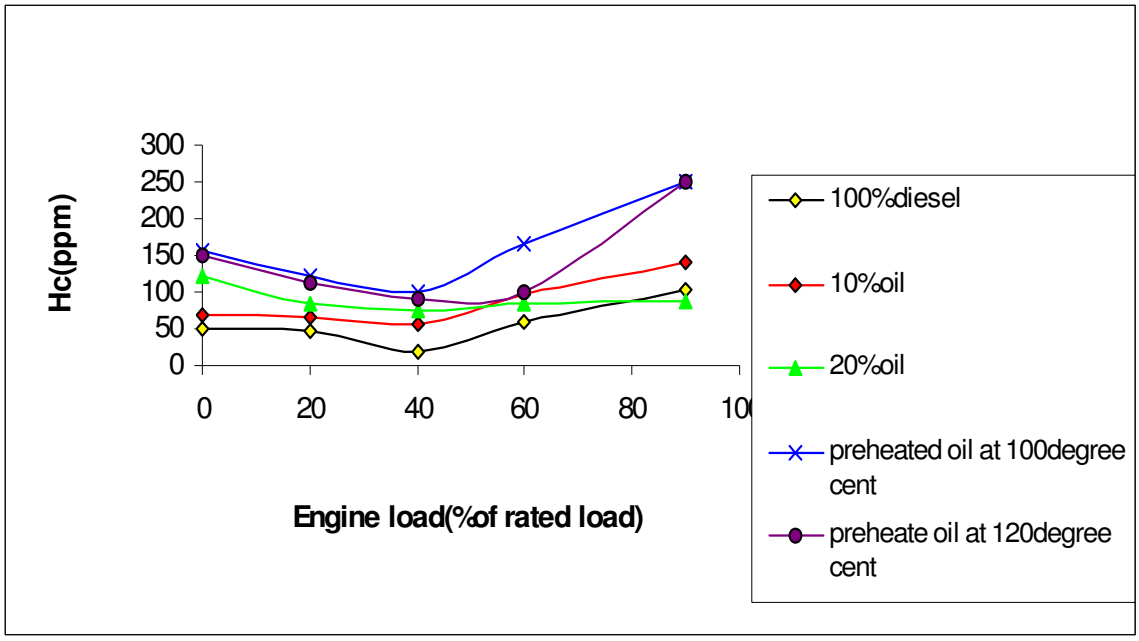

Figure 7.7 Hydrocarbon emissions vs. % engine load for the tested fuels.

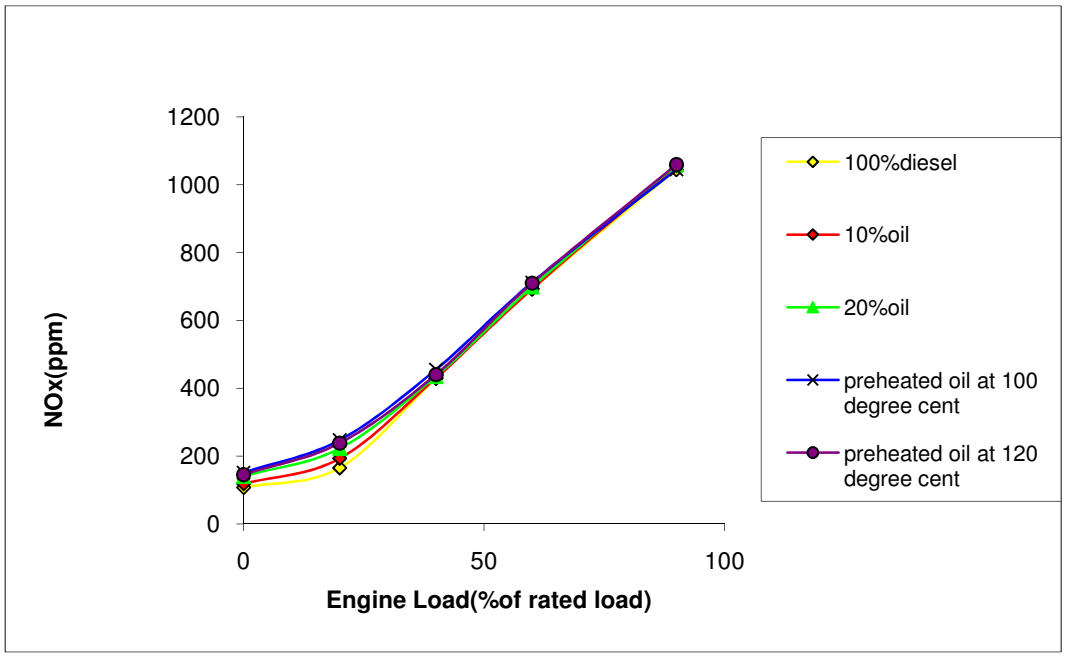

Figure 7.8 NO $_x$ emissions vs. % engine load for the tested fuels.

Oxygen content in the fuel(vegetable oil) improves the combustion and the temperature inside the cylinder is high.Nox emission will be formed more at high temperature[14]As the blend B30 is the optimum blend where the properties of fuel blend are comparable (similar) with diesel. In this blend mixing is also proper.CO emission will be formed due to poor atomization and improper mixing. Lower CO emission of bio diesel blend may be due to their complete oxidation as compared to diesel[15]

7.6. Conclusion

The main aim of the present study is to use the non-edible oil like Karanja in stationary diesel engine by reducing viscosity close to that of conventional fuel and evaluate the performance of engine with that of modified oils. The viscosity of karanja oil is reduced by preheating to 100^0C & 120^0C and blending the oil up to 20% with diesel .It is found that in the above cases the viscosity is close to that of diesel which is suitable for diesel engine. The performance tests are conducted with diesel, preheated oil and karanja oil blends at different loads and constant speed of 1500 rpm. From the experimental investigation it is concluded that the performance of 20% karanja oil in the above conditions exhibited similar performance as that of diesel without any operational difficulties. From the investigation it may be concluded that 20 % karanja oil gives better performance in comparison to other modified oil. It is also concluded that either blending up to 20% or heating the karanja oil can be used in diesel engines in rural areas for stationary applications like irrigation, processing of agricultural products and electric generation.

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8. PERFORMANCE AND EMISSION ANALYSIS OF KARANJA OIL METHYL ESTER (KOME) AND ITS BLENDING WITH DIESEL AS FUEL IN C.I ENGINE

8.1. Introduction

The biodiesel (Karanja oil methyl ester) is blended with conventional diesel in various proportions. The performance and emission characteristics of a single cylinder,5 hp, four stroke, constant speed, water cooled, direct injection diesel engine is used in stationary condition. Diesel, KOME blends [10% (B10), 20 %,(B20), 30% (B30) and 100% (B100)] are used to conduct short-term engine performance and emission tests at varying loads (0%, 20%, 40%, 60%, 80%, and 100%). Tests are carried out for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emissions of CO, CO_2, HC and NO_x gases in exhaust. The test results indicate that the blend fuel B30 can be used in the diesel engines without making any engine modifications. Also the cost of blend fuel (B30) can be considerably reduced than pure diesel. The performances of blended KOME are found to be very close to mineral diesel. Rural people can use this oil for their agricultural engines and they can reduce the requirement of diesel fuel from outside market.

8.2. Result and Discussion

8.2.1 Engine test results and discussion

8.2.1.1 Effect of brake power on brake specific fuel consumption

The specific fuel consumption of diesel, KOME and its blends at varying loads is shown in the Figure 8.1. BSFC is higher with the ester of karanja oil and its blend.

It is observed that specific fuel consumption of KOME and its blends is higher than diesel at different percentage of loads. The higher density of the KOME and its blends has led to more discharge of the fuel for the same displacement of the plunger in the fuel injection pump [1].

This is probably due to the low volatility and slightly higher viscosity of the KOME [2] which affects mixture formation of the fuel and leads to slow combustion. It is also observed that BSFC values decreases at high engine loads under all operating modes.

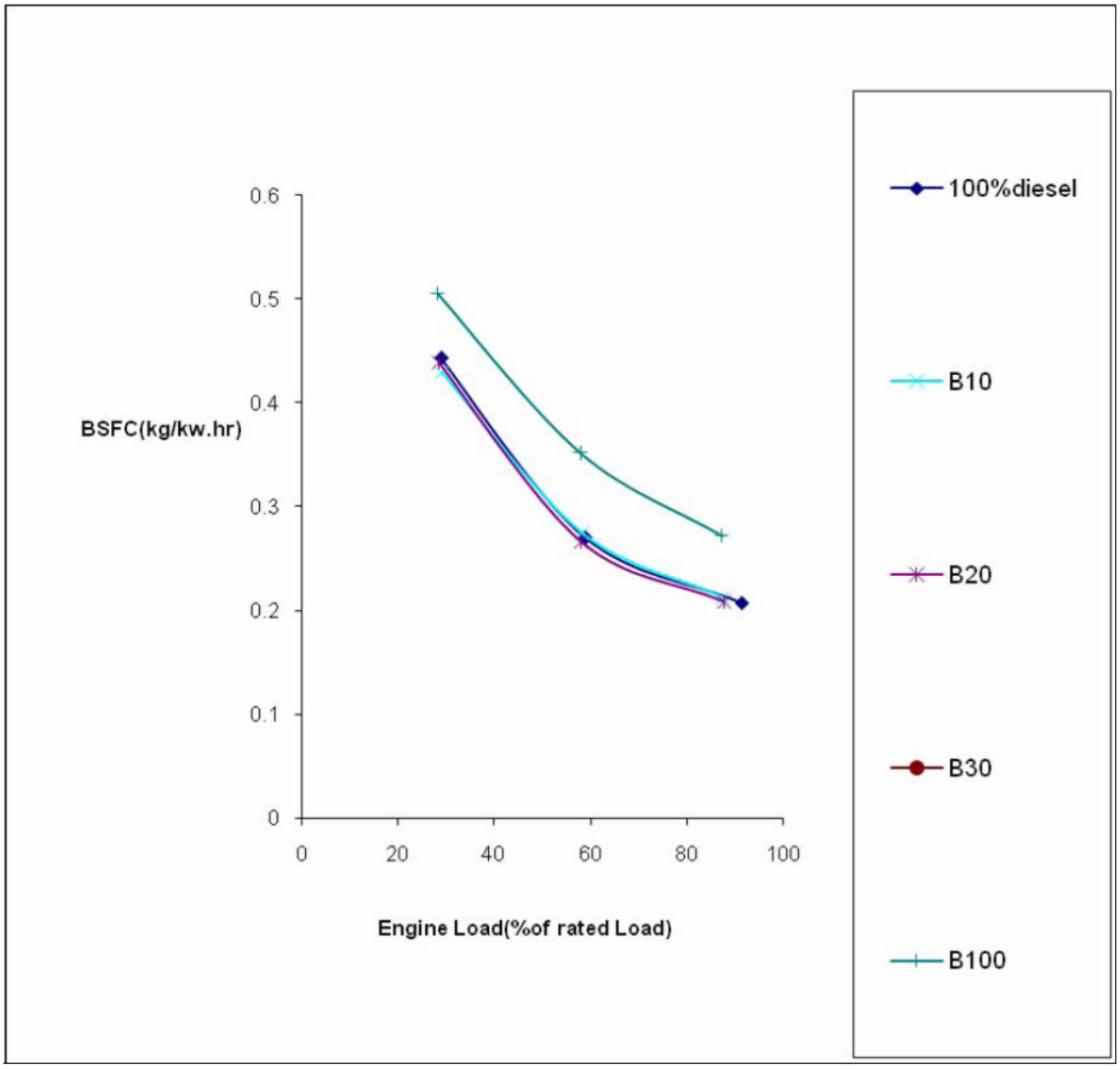

Figure 8.1 Effect of percentage of brake power on specific fuel consumption for diesel, various blends of KOME.

8.2.1.2 Effect of Engine load on brake thermal efficiency

The variation of brake thermal efficiency of the engine with load for diesel, KOME and its blends is shown in Figure 8.2. In all the cases, with increase in load the thermal efficiency increases. In most of the cases brake thermal efficiency of the KOME and its blends are lower than the diesel fuel. This is probably due to the low volatility, slightly higher viscosity and high density of the KOME [2] which affects mixture formation of the fuel and leads to slow combustion. It is also observed that brake thermal efficiency increases at high engine loads under all operating modes.

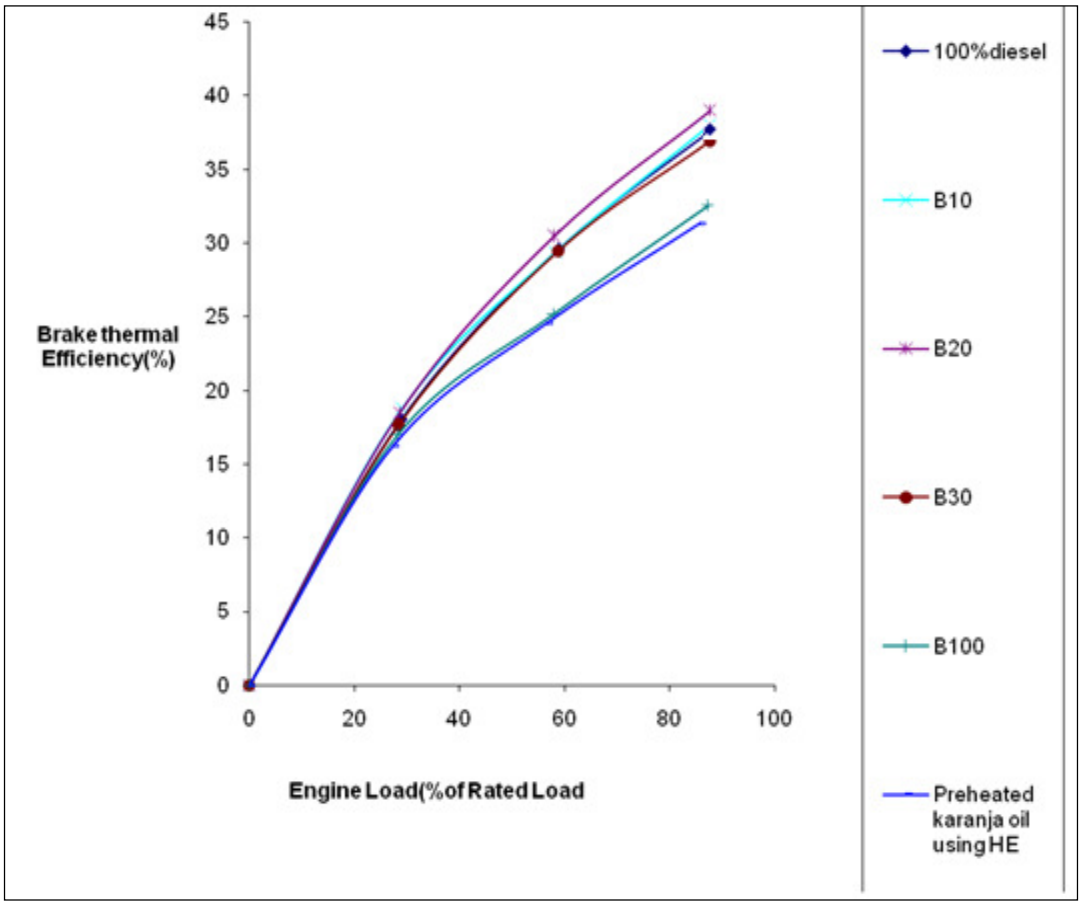

Figure 8.2 Variation of brake thermal efficiency with percentage of engine load for diesel, various blends of KOME.

8.2.1.3 Effect of brake power on exhaust gas temperature

Figure 8.3 shows the variation of exhaust gas temperature with different Engine load. The result shows that the exhaust temperature increases with increase in brake power in all cases. Exhaust gas temperature is high when the load rises and it is higher for esters and its blend than diesel particularly at higher loads. Due to incomplete combustion of the injected fuel and part of the combustion extending into the exhaust stroke, there is slight increase in exhaust temperature with KOME and its blend compared to Diesel [2].

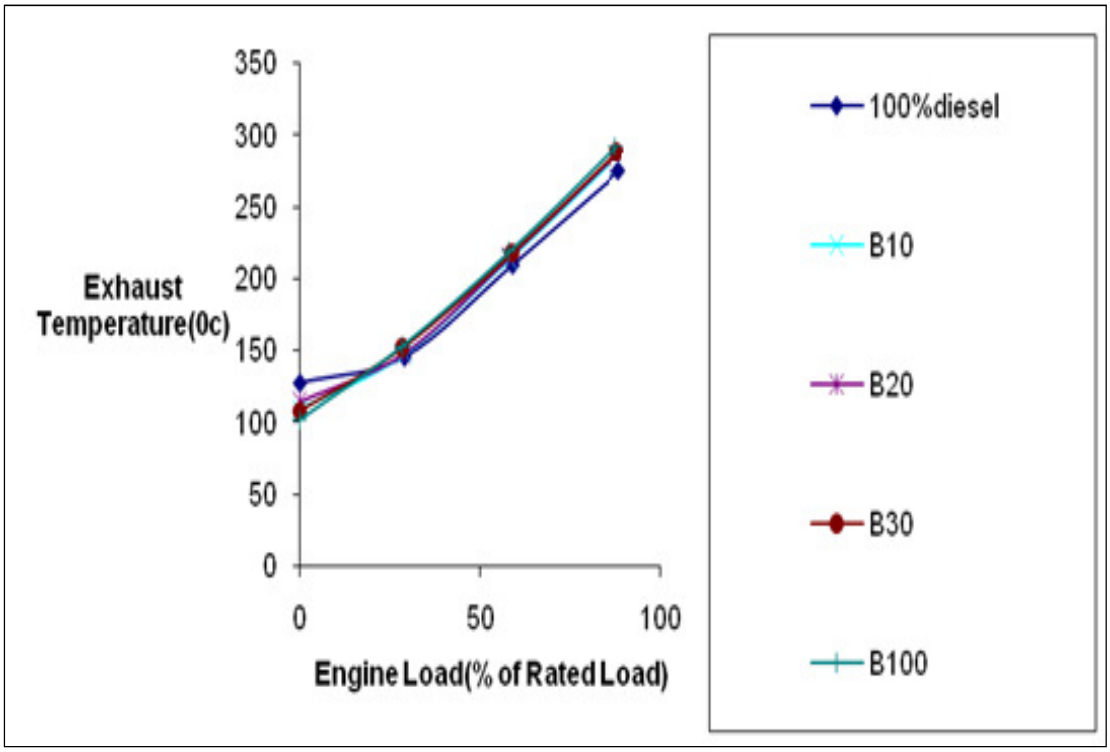

Figure 8.3 Effect of load on exhaust gas temperature for diesel, KOME and various blends.

8.2.1.4 Effect of brake power on engine Emission (Emission vs. biodiesel)

The emission results for diesel, KOME and its blends are shown in Figure 8.4–8.7. Emissions of CO, HC, and CO2 are less with KOME and its blends. The variation of smoke emission with engine load for diesel, KOME and its blends is shown in Figure 8.6. With KOME and its blends, smoke emission is higher as compared to diesel. This may be

due to the higher viscosity and density of the ester that leads to poor vaporization and slow (Incomplete) combustion of the injected fuel. When the KOME and its blends are injected, the atomization of fuel becomes poor which leads to larger droplet and less air entrainment resulting in inefficient combustion. This leads to higher smoke emission with KOME and its blends [1-2].

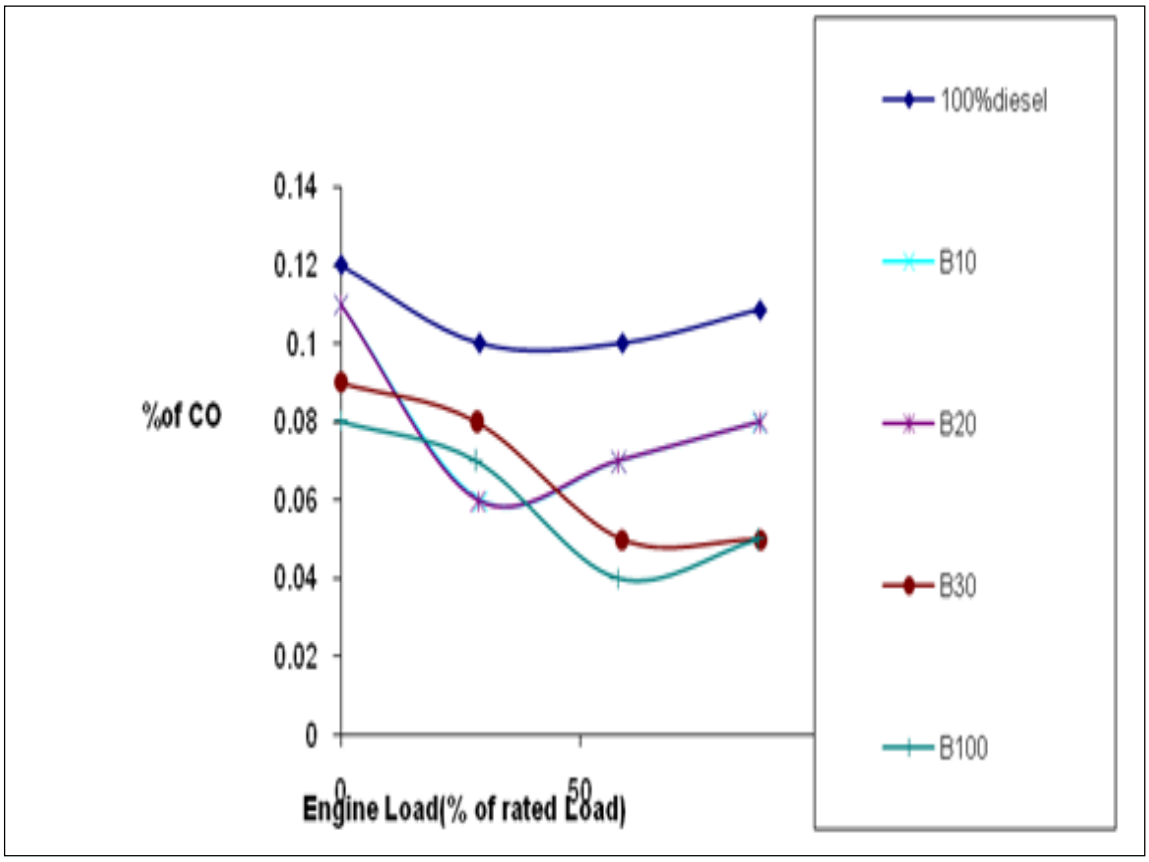

Figure 8.4 Carbon monoxide emissions Vs % engine load for the tested fuels.

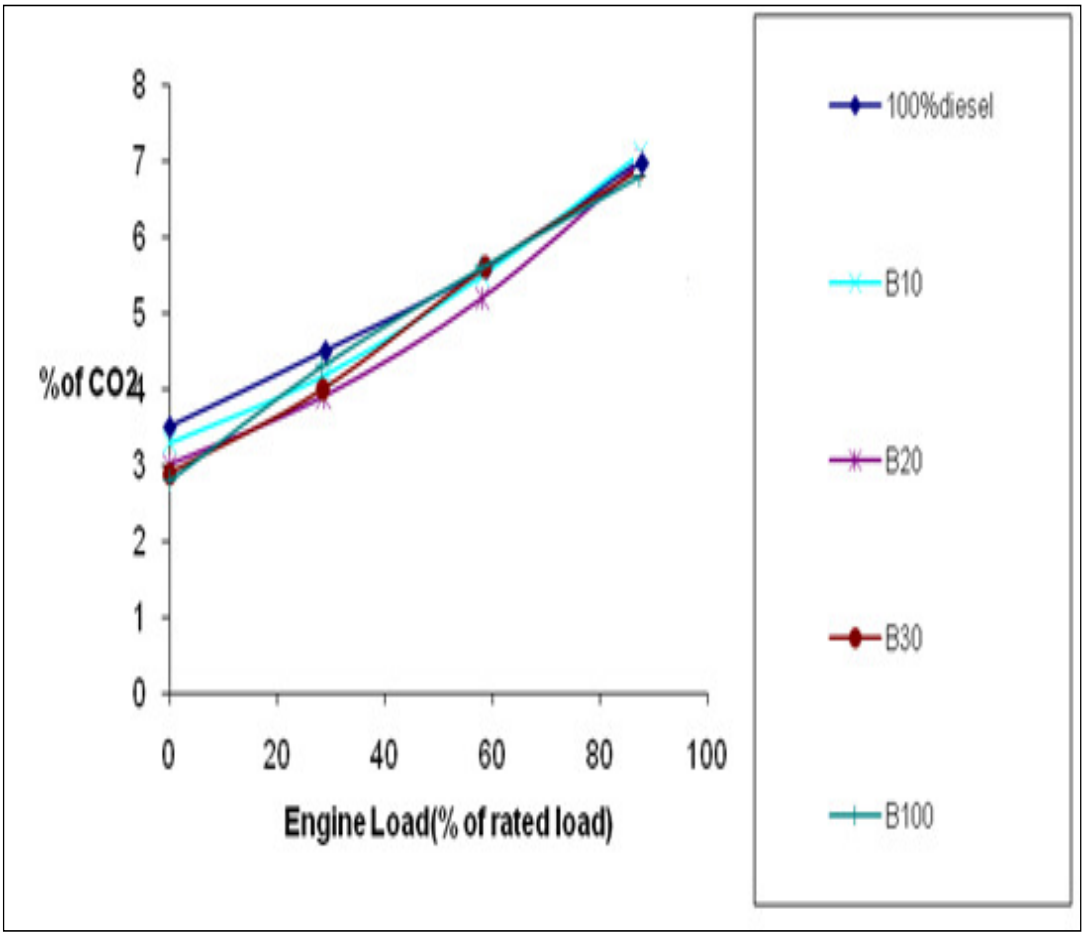

Figure 8.5 Carbon dioxide emissions Vs % engine load for the tested fuels.

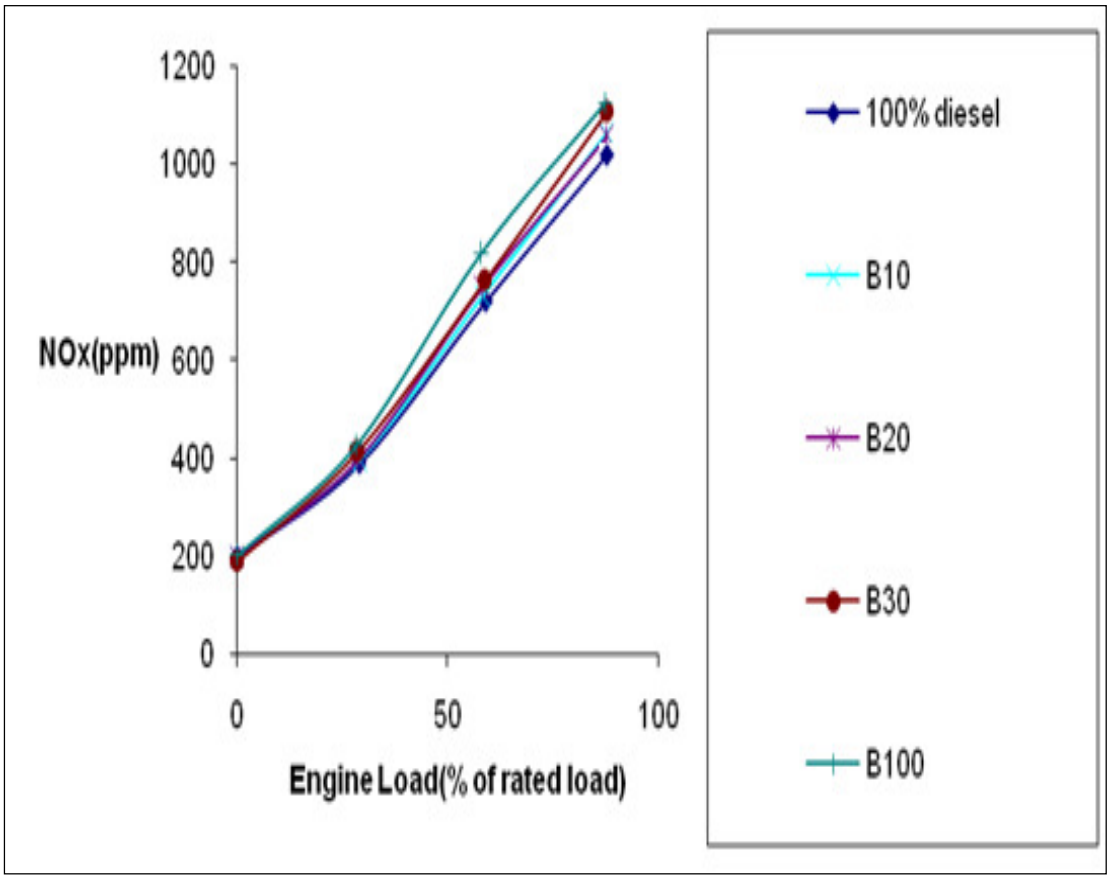

Figure 8.6 NO $_x$ emissions Vs % engine load for the tested fuels.

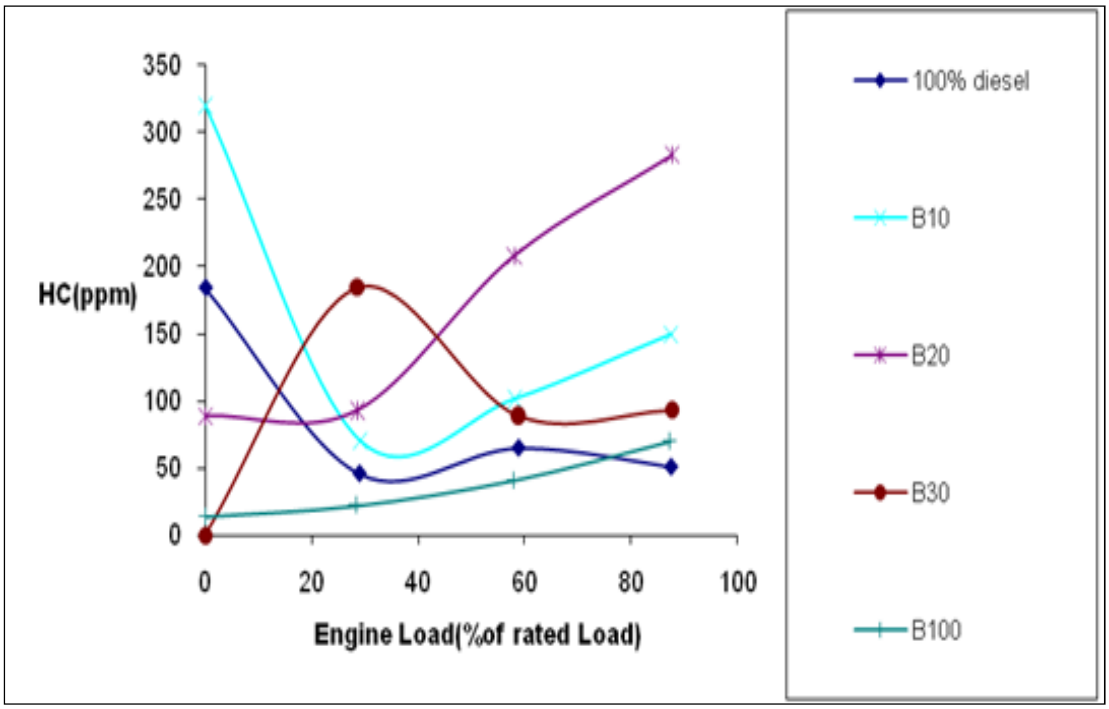

Figure 8.7 Hydrocarbon emissions Vs % engine load for the tested fuels.

8.3. Conclusion

The KOME (Biodiesel) is blended with conventional diesel in various proportions to evaluate the performance and emission characteristics of a single cylinder, 5 hp,553 CC, four stroke, constant speed, water cooled, direct injection diesel engine typically used in stationary operation. Tests are carried out for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emission of CO, CO_2, HC and NO x gases in exhaust. The test results indicate that the dual fuel combination of B30 can be used

in the diesel engines without making any engine modifications and also without any operational difficulties. The cost of dual fuel (B30) is considerably reduced than pure diesel. The performance of blended KOME is found to be very close to mineral diesel.

8.4. Reference

[1] Raju V.N, Rao G.A.P and Rammohan P. Esterified Jaropha oil as a fuel in diesel engines. I.C.Engines and combustion 2000: 65-75.

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9. CONCLUSIONS

In the present study, it is observed that the qualities of biodiesel produced from edible and non edible oil are comparable with diesel fuel. It is also observed that the specific gravities of vegetable oil methyl esters are slightly higher than that of diesel fuel. As they are slightly heavier than diesel fuel hence their viscosities are also little higher than that of diesel fuel. The heating values of these methyl esters are slightly lower as compared to diesel fuel. The fuel properties of vegetable methyl esters are also within biodiesel specifications.

A comparison is made between Theoretical and Experimental value of important chemical properties like acid value, saponification value and iodine value of non edible oils. It is found that the theoretical values are in well agreement with their corresponding experimental values. The comparison of fuel properties are made between various non edible oils (mahua, karanja and jatropha), methyl ester of non edible oil (mahua oil methyl ester, jatropha oil methyl ester and karanja oil methyl ester) with diesel. Thus this study suggests that the jatropha, mahua and karanja oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and/or transesterification. But the production of biodiesel from edible oils is currently much more expensive than diesel fuels due to relatively high cost of edible oils.

As in India the non-edible oil like *Pongamia pinnata* or Karanja oil is available in abundance, which can be converted to biodiesel. Exhaustive studies for the preparation of karanja oil methyl ester (KOME) have been done. Study was carried out with important process variables for optimization of esterification and transesterification reaction to achieve maximum bio diesel production.

Again the results demonstrate that the ANN represents a strong alternative to the extensive laboratory testing needed to find out the optimum parameters to produce biodiesel from karanja oil. In fact, simulated and experimental values are almost the same. In the present work, however, the available set of experimental data makes possible the establishment of a comparison between the experimental and estimated data, leading to a better understanding of the influence of the interactions between the reaction parameters, thus, helping to improve the esterification and trans esterification process to produce

biodiesel from karanja oil and, in summary, reducing costs and long time-consuming laboratory tests.

Further the performance and emission characteristics of karanja oil, karanja oil methyl ester and their various blends with diesel have been studied at different loads and constant speed of 1500 rpm. Tests were carried out for analyzing various parameters such as thermal efficiency, brake specific fuel consumption (BSFC), emission of CO, CO_2, HC and NO_x gases in exhaust.

In the first stage, the engine performance tests were conducted with diesel, preheated karanja oil (At 100^0C and 120^0C) and karanja oil diesel blends (10% and 20% of karanja oil). The viscosity of karanja oil is reduced by preheating to 100^0C - 120^0C and blending the oil up to 20% with diesel .It is found that in the above cases the viscosity is close to that of diesel which is suitable for diesel engine. The performance of preheated karanja oil is found to be slightly lower in efficiency due to low heating value. From the experimental investigations it is concluded that the performance of karanja oil in the above conditions exhibit similar performance to that of diesel in diesel engine without any operational difficulties. It is concluded that either blending up to 20% or heating the karanja oil can be used in diesel engines in rural areas for stationary application like irrigation, processing of agricultural products and electric generation.

In the next stage, the engine performance tests were conducted with diesel, blends of KOME in diesel [10% (B10), 20 %,(B20), 30% (B30) and 100% (B100)]. The test results indicate that the dual fuel combination of B30 can be used in the diesel engines without making any engine modifications and also without any operational difficulties. The cost of dual fuel (B30) is considerably reduced than pure diesel. The performance of blended KOME is found to be very close to mineral diesel.

This study suggests that the non-edible oils can be used as a source of triglycerides in manufacture of biodiesel by esterification and/or transesterification. The biodiesel from refined vegetable oils meets the Indian requirements of high speed diesel oil. But the production of biodiesel from edible oils is currently much more expensive than diesel fuels due to relatively high cost of edible oils. There is a need to explore non-edible oils as

alternative feed stock for the production of biodiesel. Non edible oil like mahua, karanja and jatropha are easily available in many parts of the world including India and it is cheaper compared to edible oils. The properties of biodiesel depends on the nature of the vegetable oil to be used for preparation of biodiesel and if the developed process is scaled up to commercial levels then excellent business opportunity will be offered by the biodiesel obtained from non edible oils and it could be a major step towards the creation of an eco-friendly transportation fuel that is relatively clean on combustion and provides farmers with substantial income.

10. SCOPE FOR FUTURE WORK

The production of biodiesel is greatly increasing due to its environmental benefits. However, production costs are still rather high, compared to petroleum-based diesel fuel. The introduction of a solid heterogeneous catalyst in biodiesel production could reduce its price, becoming competitive with diesel also from a financial point of view. Therefore, great research efforts are required to find the right catalysts.

The common byproducts produced while processing the biodiesel are glycerol and oil seed cake. During oil expelling, about 65-70% of the seed kernel is obtained as de-oiled cake. Glycerol is a byproduct of transesterification process. As non edible oil cake contains nitrogen, phosphorus and potassium, it can be used as organic manure. After extraction of oil from seed the detoxification of the seed cake is necessary so that the seed cake can be used as cattle feed. The type of toxic component present in the seedcake varies from seed to seed, so, seed cake detoxification is highly essential.

Glycerol is a byproduct from biodiesel industry, which is generated in large amounts during the production of biodiesel from straight vegetable oil (SVO). With every 100 kg of biodiesel produced by the transesterification of vegetable oils or animal fats, 10 kg of crude glycerol are generated. Glycerol produced is considered as a waste and has disposal problem. Moreover, waste streams containing high levels of glycerol are generated in almost every industry that uses animal fats or vegetable oils as the starting material.

Despite of the wide applications of pure glycerol in food, pharmaceutical, cosmetics and many other industries, it is too costly to refine the crude glycerol to a high purity. The crude glycerol, the low-priced byproduct of biodiesel industry, can be efficiently used for the production of additional value-added products like 1, 3-propanediol, acrolein, polyglycerol, tartonic acid, hydrogen, synthesis gas and liquid chemicals etc. The production of value-added chemicals from glycerol may lead to a decrease in biodiesel prices. Furthermore, it will improve glycerol market. The production of biodiesel from vegetable oils provides numerous local, regional and national economic benefits. To develop biodiesel into an economically viable and significant option across the world, it is required to ensure good prices for byproducts.

More intensive investigation are required for exploring different valuable byproducts from glycerol and proper utilization of oil cake is required to make biodiesel production into an economically viable enterprise.

BIO-DATA

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List of Publications

Paper Published/Accepted in National and International Journal

1. Basanta K. Sahu, Saroj K. Padhi,R. K. Singh and G.K.Roy "Effect of a rod promoter on velocity in a square gas-solid fluidized bed "Chemical Engineering World, April 2008, pp. 53-57.
2. Padhi SK, Singh R K, "Characterization of Jatropha oil for the production of Bio diesel " Natural Product Radiance (NPR) vol 8(2) March-April 2009
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5. Padhi SK, Singh R K, "Hydrodynamic Studies of Gas-Solid Fluidization in Hexagonal Bed for Non-spherical Particles " Journal of scientific and Industrial Research. (Vol. 68, November 2009 pp.951-95 4)

Paper Published in National and International Conferences

1. Padhi SK , Singh RK, "Kinetic studies for preparation and characterization of mahua oil methyl ester". In International conference on Bio-Fuels Vision 2015,October 13-15,2006 organised by Engineering college Bikaneer.
2. Padhi SK, Singh R K "Characterization Of Mahua Oil (Madhuca Indica) For The Preparation Of Biodiesel (Mahua oil methyl ester) "International conference on Advances in energy research 12th to 14th December 2007,organised by Indian Institute of Technology (IIT) Bombay,India and Published by McMillan.
3. Padhi SK, Singh R K "Preparation and characterization of Bio diesel from tree borne oilseeds (TBOs)" International Conference on Advances in Mechanical Engineering – 2009 , during 3-5 August 2009 , organised by SVNIT Surat,India.
4. Khan Mohd. Yonus Padhi SK, Singh R K "Performance of a C.I. Engine running on 20/80 Blend of Different Vegetable Oils and Diesel" International Conference on Advances in Mechanical Engineering – 2010 , during 4-6 January 2010 , will be organised by SVNIT Surat,India
5. Khan Mohd. Yonus, Nafees Ahmad, Khan Mohd. Nasir, and Padhi Saroj Kumar, Characterization of used Sunflower Oil (USO) For Utilization As CI Engine Fuel, All India seminar on catalyzing vision 2020:Challenges of Indian Chemical Engineers(CV-2020),Jan.2007,Organised by Department of Chemical Engineering,National Institute of Technology, Rourkela.
6. Padhi SK, Singh R K "Biodiesel -The Green Energy" ALL INDIA SEMINAR on 'ENERGY, ENVIRONMENT & ECONOMICS (EEE 2007)' organized by National Institute of Technology, Rourkela, Orissa.